Structural Uses for Ductile Ordered Alloys

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A number of possible generic applications are suggested for the newly developed ductile ordered alloys, including applications in gas turbine engines, rocket propulsion

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Finally, it is concluded that the properties of the newly developed ductile ordered alloys appear to be sufficiently promising to warrant a coordinated program for the application of these alloys to be undertaken.

STRUCTURAL USES FOR DUCTILE ORDERED ALLOYS

Report of the
Committee on Application Potential for
Ductile Ordered Alloys

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

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CONCLUSIONS AND RECOMMENDATIONS

Ordered alloys have a number of properties that make them extremely attractive for structural uses, particularly at elevated temperatures. Ordered alloys have other very important uses, for example, as superconductors; however, only structural uses will be discussed in this report. Since many of them show both a high yield strength and high modulus along with a low density at elevated temperatures, their specific modulus and specific strengths are very attractive when compared to those of other materials. The work hardening rate of ordered alloys also is quite high compared to that of disordered alloys. The self-diffusion rate of these alloys is low compared to that of disordered alloys; therefore, properties that are determined by self-diffusion rate also can be quite different. For example, since the steady state creep rate is directly proportional to the self-diffusion rate, the creep rate of ordered alloys is slower than that of disordered materials. Thus, ordered alloys are stronger (deform more slowly) at elevated temperatures than do disordered alloys. Ordered alloys also tend to have longer high cycle fatigue lives at room temperature than do disordered alloys; however, this improvement has not been documented at elevated temperatures, except under crack growth conditions. Finally, the oxidation resistance of many ordered alloys, particularly the aluminides, is very high.

Ordered alloys, however, have rather low ductilities and, as a result, they traditionally have been used in structural applications only as second-phase particles added to strengthen the disordered matrix, as, for example, in nickel-base superalloys. The reasons for the low ductility of ordered alloys are quite diverse; they include an insufficient number of slip systems (primarily in noncubic alloys), a limited cross slip, impurity locking of dislocations, and intrinsically brittle grain boundaries.

Recent work at a number of different laboratories, however, has shown that the ductilities of ordered alloys can be dramatically improved by the

intelligent application of physical metallurgical principles. Ductilities have been improved by the removal of impurities and second-phase particles; by alloying to transform a noncubic to a cubic structure and thereby increase the number of available slip systems; by grain refinement through thermal-mechanical treatments; by rapid solidification through the melt spinning technique to produce ribbons, or the rapid solidification rate (RSR) technique to produce powders (which are subsequently processed by powder metallurgical techniques); or by microalloying with boron to improve grain boundary cohesion. As a result of these efforts, a new class of single-phase ductile ordered alloys (or possibly multiphase alloys with an ordered matrix) is now possible. These alloys show promise of offering extremely good properties at elevated temperatures while not suffering from the ductility problems previously encountered in these alloys.

Although it is clear that the ductilities of ordered alloys can be dramatically improved, no one method is a panacea. Physical metallurgists have learned that a variety of treatments can improve the ductility of ordered alloys but, without detailed experimentation on a given alloy, they do not yet know enough to decide which treatment will be effective for that particular alloy. Furthermore, they do not yet know why some of these ductilizing treatments succeed. For example, small additions of boron to Ni_3Al result in dramatic improvements of the grain boundary strength, but this effect is found only if the alloy is slightly aluminum-deficient. The mechanism by which boron improves the grain boundary strength and, furthermore, why it does not operate in many other grain boundary-brittle ordered alloys is simply not understood.

The number of research programs in the United States that concentrate on ordered alloys is rather small, particularly when compared to 15 years ago when there were many more programs in both industrial and university laboratories. An extensive, long-term program at the Air Force Wright Aeronautical Laboratories under the direction of Harry A. Lipsitt has produced impressive results leading to possible practical applications of several aluminides. Another successful program is underway at Oak Ridge National Laboratory (ORNL) under the direction of C. T. Liu; Ni_3Al and Co_3V are being studied, and Ni_3Al-based alloys with remarkably high ductility and strength have been developed. Additional Department of Energy (DOE) supported work on Ni_3Al is also being performed at Dartmouth University. The National Aeronautics and Space Administration, Lewis Research Center for the Conservation of Strategic Aerospace Materials (COSAM) program also supports research on several aluminides at NASA-Lewis and at Texas A & M, Stanford, and Dartmouth Universities. Also the Office of Naval Research (ONR) supports programs at Ohio State University, General Electric Company, and ORNL. Smaller programs are being conducted at the University of Pennsylvania (Pope and Vitek) with National Science Foundation (NSF) funding, at Rensselaer Polytechnic Institute (Stoloff) with DOE and ONR funding, and at Michigan Technological University. Thus, we can conclude that the U.S. effort in this area is rather small, but possibly growing.

The level of effort in Japan is modest but appears to be increasing quite rapidly. Some information to support this conclusion appears in the literature, but it is based primarily on conversations between members of this committee and their Japanese colleagues who have stated that there is

now a concerted effort being made in Japan to develop a new class of
high-temperature materials based on ordered alloys. A large number of
Soviet researchers are working on ordered alloys, but one can only speculate
as to whether any work is being performed to produce ductile ordered alloys
since this kind of work may not be reported in the open literature. Only a
few ordered alloy research programs are being conducted in Europe. There is
a program on titanium aluminides at the National Gas Turbine Establishment
in Farnborough in the United Kingdom, and there are three programs at
universties at Groningen, Holland, under de Hosson; at Poitier, France,
under Rabier; and at Lille, France, under Escaig. The university programs
are highly scientific in nature and are aimed at developing an understanding
of the basic physical phenomena rather than at developing particular alloy
systems.

The committee believes, based on its survey of research in progress,
that, while the U.S. research effort is much smaller than it was 15 to 20
years ago, it is highly productive and appears to be ahead of other programs
being carried out in other parts of the world.

For early applications, in systems whose preliminary design and
performance requirements have already been established, it must be
recognized that a new alloy with better properties than an existing alloy
will be used only if it allows the designer to meet performance
specifications at lower cost or if use of the new alloy is necessary to meet
the specified performance. For future designs, a new alloy may permit
establishment of higher system performance requirements and thus become the
necessary material of choice. However, even on currently designed systems
there are windows of opportunity for new alloys wherein these may be
substituted for others in the design stage (to reduce unanticipated weight
gains, for example). Opportunities may also be presented during prototype
testing or to correct a service problem.

Before any alloy is incorporated into a system it will normally have
gone through the stages of laboratory demonstration, development (including
processing development where large costs are incurred), and finally,
qualification. An adequate body of data must be available when
qualification testing is required in order to support a decision to
undertake such testing and the high costs involved.

The titanium aluminides developed under Air Force sponsorship are well
along the path towards usage, but development of the iron aluminides and the
ductile nickel aluminides has proceeded only to the laboratory stage with
some processing work only recently begun.

The committee proposes that these new materials be considered for
application in rotating parts of gas turbine engines because of their low
density, high strength, and high oxidation resistance at elevated
temperatures. Also, if these new materials show improved thermal and
high-cycle fatigue resistance at elevated temperatures, they could be used
as a turbine blade material in gas turbine engines in rocket propulsion
systems. The combination of high strength at elevated temperatures and low
density also suggests a number of applications to space power systems.

Before the designer can consider using a new material he must have considerable information on the engineering properties of the material, including data on its physical properties, time-independent and time-dependent properties, environmental compatibility, and fabricability. The data base for titanium aluminides is rather large but it is much more limited for iron aluminides and even more limited for nickel aluminides. In fact, virtually no data of the type required by a designer are available on the ductile iron and nickel aluminides.

Since ductile ordered alloys show such unusual promise, the committee recommends that a three-phased program be initiated in which some of the engineering properties of ductile iron and nickel aluminides are measured, cost trade-off studies then are performed, and, if the potential cost and performance advantages of these alloys are clear, additional properties are measured. In the first phase, physical properties, tensile properties, creep and creep-fatigue properties, toughness, crack growth properties, and corrosion properties should be measured on heats of sufficient size that several laboratories can perform experiments on the same material. This phase should be relatively inexpensive compared with the second and third phases. If the results of Phase I show that these alloys have sufficient promise, Phase II should be started in which both experimental and production lots of material are tested, materials processing optimization is undertaken, the effects of multiaxial stress states and product anisotropy are studied, joining techniques are investigated, and compatibilities with various environments are studied. Phase III should involve testing of multiple production runs of material, development of statistical distributions of mechanical property data, and the development of specifications.

To date there has been very limited work done on the processing of ductile ordered alloys. Based on the limited information available in the literature, a wide range of primary processing methods are available for the production of ordered alloys, including various melting and casting techniques, several deformation processing methods, and powder metallurgy (PM) methods. The best primary processing route for ordered alloys has not yet been identified and this must be done in Phase II of the program recommended above. Primary processing is followed by secondary processing when the product is made into its final shape (bar, sheet, rod, etc.), and no work has yet been performed on aluminides to determine the optimum secondary processing steps to be followed to provide the best properties at the lowest cost.

Although work is under way to provide the kinds of information required by producers and designers, the development of ductile ordered alloys is very much based on the science of these materials, and a great deal of scientific information about these materials is still needed. Needed are additional phase diagrams; data on the effects of order and ordering kinetics on properties; an understanding of the deformation behavior of binary, ternary, and higher order systems including the effects of fault energies, dislocation cores, and domain structures; an understanding of grain boundary properties including the effects of impurity segregation; diffusion data; and an understanding of the effects of point defects.

Finally, a number of other ordered alloys have not yet been considered for structural usage. For example, ordered alloys having long period superlattices in which periodic faults exist have not yet been examined for such usage, but since the period of the fault spacing can be changed by alloying and since the mechanical properties are expected to depend strongly on that spacing, these alloys are good candidates for future consideration.

Over the longer term, the committee expects that quantum mechanical calculations of equilibrium properties of ordered alloys will have a major impact on the development of additional alloys. Since only some of the trends in properties with changes in composition, state of long-range order, and defect structure, are understood, the development of new alloys is necessarily Edisonian in nature. The additional predictive capabilities of such calculations are expected to be invaluable in future development programs.

SUMMARY

1. In the past, interest in ordered alloys has been limited by problems of brittleness and inadequate creep resistance, but recent work on a number of alloys has suggested that these problems can be overcome.

2. Ordered alloys potentially provide a combination of properties which are of great interest for DOD applications, particularly for high temperature load-bearing structures (i.e., in gas turbine engines, rocket propulsion systems, and space power systems).

3. The fact that high-strength ductile aluminides have been developed after only limited research on a few compositions suggests that there is potential for the development of even better systems with the application of a coordinated research effort.

4. A development program is recommended in which engineering property and processing data are gathered in a phased manner, and after each phase, cost and performance analyses are performed to see if further phases in the development are justified.

5. Areas of further scientific investigation of ordered alloys are suggested which can form the basis for the development of future ordered alloys of practical interest.

CONSTITUTION, PROPERTIES, AND CURRENT STRUCTURAL USES

INTRODUCTION

Ordered alloys are alloys in which there are two or more atomic species and the different atomic species occupy specific sites in the crystal lattice. Such alloys tend to occur at well defined atomic ratios (i.e., AB, A_3B, AB_3, etc.). The tendency for segregation to the different atomic sites depends, in many cases, on temperature. For example, at low temperatures CuZn and Cu_3Au have the ordered structures shown in Figure 1, but above a critical temperature (T_c), the atoms become randomly mixed on the different atomic sites and become random solid solutions. The ordered structure shown in Figure 1a is called the B2 (or $L2_0$) structure and that in Figure 1b, the $L1_2$ structure.

The existence of ordered alloys as discrete entities was not established until 1839 (Westbrook 1967). However, for many hundreds of years ordered alloys have, in fact, been utilized for their interesting mechanical and physical properties. One may cite two examples: (1) dental amalgams, alloys of Ag, Sn and Hg that consist of a mixture of Ag_2Hg_3 and Sn_6Ag, were first described in 659 AD (Chu 1958), and (2) high tin bronzes, containing principally $\delta CuSn$, were utilized by the Romans, and the Chinese as early as 1800 BC (Schweiz 1973). Westbrook (1967) cites other uses such as type metal based upon SbSn, ship sheathing made from β brass, and statuary made from ϵ brass. Magnetic and superconducting materials based on ordered alloys also are well known, especially the Heusler alloys (Cu_2MnAl) and various superconductors such as V_3Ga and Nb_3Sn.

An early indication of fracture problems with ordered alloys in the eighteenth century may be found in the work of Geoffroy (1725), who noted a difference in the fracture characteristics of various phases of copper and zinc. One of the earliest systematic studies of the mechanical behavior of ordered alloys is that of Kurnakov and Zhemchuzhnii (1908). Tammann and
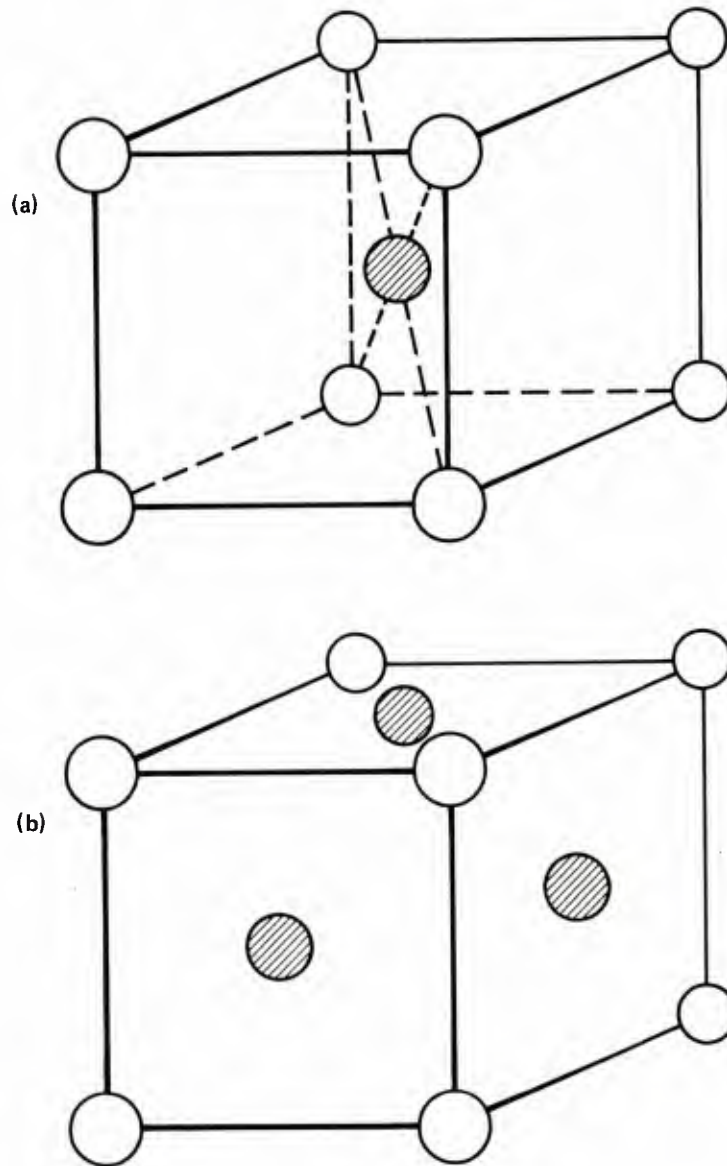
FIGURE 1 (a) At low temperatures: CuZn has the cesium chloride B2 long-range-ordered structure and (b) Cu₃Au has the face centered cubic-based L1₂ structure.

Dahl (1923) showed that ordered alloys have a ductile-to-brittle transition temperature, and Lowrie (1952) later observed that the onset of ductility occurs in the temperature range $T/T_m \sim 0.61-0.68$, where T_m is the melting point in °K. Westbrook and Wood (1963) showed that grain boundary embrittlement is a common feature of many ordered alloys and that the embrittlement could be related to excess hardening near the grain boundaries.

Ordered alloys [e.g., Fe-Mn-Al (Gibson 1960)] were seriously examined as potential structural materials by many investigators in the 1950s, and subsequent years saw intensive research to examine their mechanical behavior. Beneficial effects of long range order in suppressing diffusion controlled phenomena (e.g., creep, recrystallization, and, in the case of the aluminides, oxidation) were identified in extensive reports by workers in the Soviet Union, Great Britain, and in the United States. However, little success was achieved in improving the ductility of polycrystals of many of the most interesting systems, most notably aluminides based on titanium, iron, and nickel. During the same period, it was noted that many of these alloys were ductile when all grain boundaries were eliminated. However, the use of single crystals in high-temperature applications such as gas turbines was not seriously considered until about 1970, by which time little additional research on ordered alloys was being carried out in this country. Rather than attempting to use ordered alloys in structural applications, metallurgists identified other uses for them in which brittleness was not a problem or, at least, could be minimized. One example was the use of nickel and cobalt aluminides as thin coatings on turbine hardware; another was the use of Fe-Si alloys (Sendust) as elements of sound reproduction systems. The use of high-permeability Fe-Co alloys in transformers also can be cited. In addition, ordered alloys such as Ni_3Al (γ') and Ni_3Nb (γ'') were extensively used as distributed phases to strengthen nickel-base superalloys whereas Ni_4Mo and other compounds were utilized as strengthening phases in maraging steels. In the case of nickel-base superalloys, the volume fraction of γ' steadily increased from near zero in the 1940s to more than 60 percent in modern alloys. This was accomplished by adding increased quantities of aluminum as well as titanium, niobium, and tantalum, all of which are soluble in γ', and by vacuum melting.

Interest in utilizing ordered alloys for structural applications was reawakened in this country when researchers at Wright-Patterson Air Force Base (together with contractors sponsored by the Air Force) discovered that ductility improvements could be achieved in TiAl- and Ti_3Al-base alloys using a combination of powder metallurgy and alloying techniques. The development of rapid solidification methods (RSR and melt spinning, in particular) led to renewed interest in the iron and nickel aluminides. Finally, several exciting discoveries were reported that permitted substantial ductility to be achieved in cast and wrought ordered alloys previously known to be extremely brittle. The first of these accomplishments involved replacing cobalt in Co_3V with nickel (Liu 1973) and then iron (Liu 1979), leading to a series of face-centered cubic Ll_2-type superlattices with extensive ductility at ambient

temperatures. It was found that ordered structures can be altered systematically through the control of electron-to-atom concentration in alloys. This can be achieved by partial replacement of cobalt and nickel with iron, which lowers e/a and stabilizes the ordered structure. $(Fe,Co,Ni)_3V$ alloys with the cubic ordered structure are ductile, with tensile elongation exceeding 35 percent at room temperature (Liu 1984). Shortly after the first reports of this achievement at ORNL, it was reported in Japan that polycrystalline Ni_3Al could be made ductile by adding small quantities of boron (Aoki and Izumi 1979). Single crystals of many aluminides are quite ductile but their polycrystalline forms are not. The brittleness of such polycrystalline materials is associated with weak grain boundaries that cause brittle intergranular fracture without much plastic deformation within the grains. Small amounts of dopants, such as boron, and thermomechanical treatments can suppress brittle grain boundary fracture (Liu 1984). The critical composition range over which boron was beneficial was identified at ORNL (Liu and Koch 1982). These discoveries, together with the national search for replacements for strategic metals such as cobalt and, possibly, chromium and the need to develop energy-efficient propulsion systems, have in the past year or two stimulated much additional work--largely in the area of improving low temperature ductility and increasing high temperature strength--in this country, Japan, and Western Europe. Soviet publications on ordered alloys have been voluminous, but there is little visible evidence to date of Soviet progress in developing such alloys for structural applications; rather, Soviet research has emphasized alloy theory, yielding and strain-hardening phenomena, and the use of various imaging techniques to aid in the study of crystal structure and crystal defects.

The characteristics that render ordered alloys so interesting as bases for alloy development will be discussed below as will their current status and applications.

CHARACTERISTICS OF ORDERED ALLOYS

The formation of long-range order in alloy systems frequently produces a significant effect on mechanical properties, including elastic constants, yield and tensile strengths, strain-hardening rates, ductility, and resistance to cyclic or static (creep) deformation (Lawley 1967, Stoloff 1971, Stoloff and Davies 1966). In some ordered systems, there is a change in crystal structure at the order-disorder transformation, leading to property changes dependent chiefly on stresses generated by the transformation. More widely studied and significant, however, are the properties of alloys in which: (1) there is no lattice change with ordering but only a rearrangement of atoms on lattice sites, (2) atoms rearrange from a body centered or face centered cubic to simple cubic, or (3) no order-disorder transition occurs below the melting point of the alloy. Table 1 identifies the most common superlattice types and presents information concerning dislocation types.

Elastic Constants

In some ordered alloys (e.g., Cu_3Au), the elastic constants change discontinuously at T_c (Siegel 1940); in others (e.g., β-brass), there

TABLE 1 Dislocation Morphologies in Some Ordered Alloys

Superlattice Type (Strukturbericht Designation)	Chemical Designation	Unit Cell Dimensions	Alloy Types	Superlattice Dislocation Type	Burgers Vector of Each Dislocation	Antiphase Boundary Type[a]
B2	CsCl	a_o	NiAl, AgMg AuZn		$a_o\langle100\rangle$	None
			CuZn, FeCo FeAl, FeRh NiAl, AgMg AuZn		$1/2a_o\langle111\rangle$	NN
DO$_3$	Fe$_3$Al	a_o	Fe$_3$Al, Fe$_3$Si Fe$_3$B		$1/4a_o\langle111\rangle$	NN NNN
Ll$_2$	Cu$_3$Au	a_o	Cu$_3$Au, Ni$_3$Mn Ni$_3$Al, Ni$_3$Fe Cu$_3$Pd, Ni$_3$Ti Ag$_3$Mg, Ni$_3$Ta Ni$_3$Si, Cu$_3$Pt Ni$_3$Ga		$1/6a_o\langle112\rangle$	NN NN+SF
DO$_{19}$	Mg$_3$Cd	a_o c_o	Mg$_3$Cd		$1/6a_o\langle10\bar{1}0\rangle$ $1/2a_o\langle2\bar{1}\bar{1}0\rangle$	NN SF NNN
Ll$_o$	CuAu	a_o c_o	CuAu, CoPt FePt		$1/6a_o\langle112\rangle$	NN NN+SF SF

(Source: Marcinkowski 1974)
[a]NN, nearest neighbor; NNN, next-nearest neighbor; SF, stacking fault.

is a continuous change in the elastic constants upon passing through T_c (Good 1941). Young's modulus for β-brass and related alloys increases continuously with degree of order. Usually, the change in elastic constants with order is small (in the range of 3 to 10 percent) and, therefore, changes in other mechanical properties arising from ordering are seldom controlled by effects on elastic constants. Rather, the principal effects of ordering on mechanical properties arise from changes in dislocation configurations due to the added constraints that ordering places on the nucleation and motion of dislocations.

One of the attractive features of aluminides such as TiAl and Fe_3Al in structural applications is the high specific modulus. For example, the specific modulus of a boride-strengthened Fe_3Al alloy recently has been reported to be 50 percent higher than that of A-286 (a widely used Fe-base alloy containing Ni_3Ti precipitates) between 25°C and 760°C (Figure 2) (Ray et al. 1983). Modulus data for several of the B2 aluminides (Wolfenden and Harmouche 1983) and TiAl and Ti_3Al (Schafrik 1977) suggest that high stiffness/density ratios are characteristic of the aluminides.

Some representative Young's modulii, melting (T_m) and critical (T_c) temperatures, and densities are shown in Table 2 for a number of ordered alloys, including the aluminides.

TABLE 2 Properties of Intermetallic Compounds

Alloy	Structure	Young's Modulus (10^6 psi)	T_m(°C)	T_c(°C)	Density (g/cc)
TiAl	Ll_0	25.5	1460	1460	3.91*
Ti_3Al	DO_{19}	21.0	1600	1100	4.2**
NiAl	B_2	42.7[a]	1640	1640	5.86*
Ni_3Al	Ll_2	25.9[e]	1390	1390	7.50*
FeAl	B_2	37.8[b]	1250-1400	1250-1400	5.56*
Fe_3Al	DO_3	20.4[c]	1540	540	6.72*
CoAl	B_2	42.7[b]	1648	1648	6.14*
Zr_3Al	Ll_2	19.6[f]	1400	975	5.76*
Fe_3Si	DO_3	39.4[d]	1270	1270	7.25*
Co_3V	hex	---	1400	1070	7.92**
$(Fe_{22}Co_{78})_3V$	Ll_2	---	1400	950	7.80**
$(Fe_{60}Ni_{40})_3$ $(V_{96}Ti_4)$	Ll_2	---	1400	680	7.60**

*Calculated from lattice parameter data.
**Estimated.
[a]Schafrik 1977
[b]Wolfenden 1983
[c]Morgand et al. 1968
[d]H. A. Lipsitt unpublished
[e]Stoloff and Davies 1965
[f]Turner et al. 1978
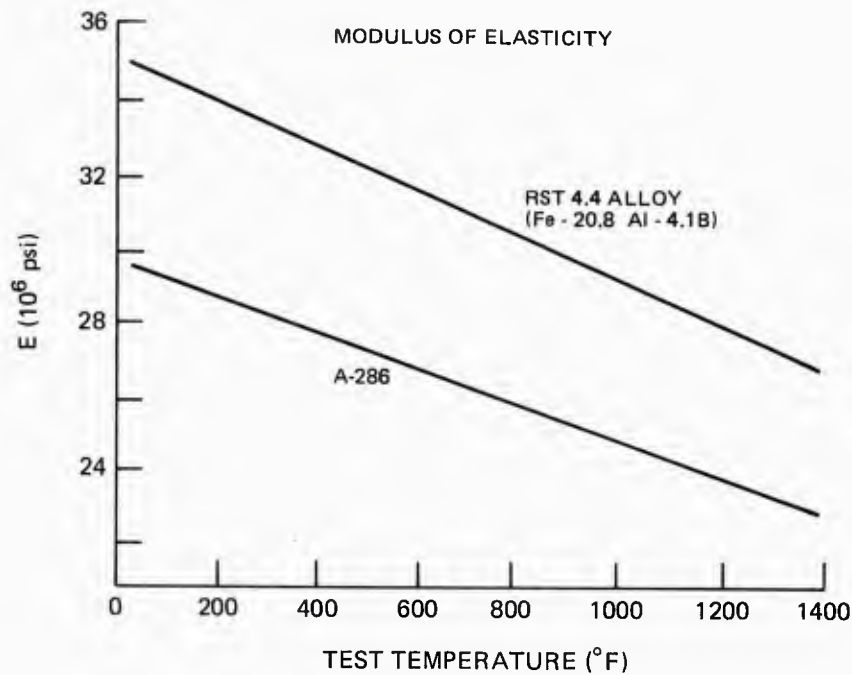
FIGURE 2   Elastic moduli of Fe-20.8, Al-4.1B, and A-286 (Ray et al. 1983).

Superlattice Dislocations and Antiphase Boundaries

Since an ordinary (unit) dislocation moving in a superlattice cannot
recreate the crystal structure in its wake, disorder in the form of an
antiphase boundary (APB) will result from the motion of such a dislocation
(Marcinkowski 1963). The additional energy of the APB can be eliminated,
however, by motion of dislocations in groups such that no net change in
order occurs behind the dislocations. These groups, which consist of two or
more dislocations connected by a strip of APB or other planar fault, are
known as superlattice dislocations. Within the superlattice dislocation,
each unit dislocation may further dissociate into its constituent partial
dislocations (as listed for various superlattices in Table 1). Therefore,
the stacking fault energy of the alloy plays a role in determining the
dislocation fine structure. The appearance of slip bands intersecting a
polished surface is quite different in alloys in the ordered and disordered
states. Many ordered alloys reveal diffuse slip on only one or a few slip

systems and cross slip is restricted, thereby leading to brittleness, whereas coarse slip steps are observed in the disordered condition. It is the motion of superlattice dislocations and their interactions with each other and with obstacles such as grain boundaries, precipitate particles, or grown-in antiphase boundaries that control the mechanical behavior of ordered alloys. However, an exception to this behavior is noted in Ni_4Mo, which rarely exhibits superlattice dislocations at room temperature. When superlattice dislocations are observed in Ni_4Mo, they consist of five identical unit dislocations (Nesbit and Laughlin 1980).

Antiphase boundaries, which are produced during heat treatment, separate domains that may be perfectly ordered within themselves but are out of step with one another. These thermal antiphase boundaries can be made to grow by appropriate annealing treatments. During the early stages of an isothermal ordering treatment, antiphase domains (APDs) generally are very small and may not be in contact with each other. However, with continued annealing, the APDs will impinge on each other and may grow to a size limited by the specimen size (in single crystals) or the grain size (in polycrystals). In some cases, (e.g., Ni_3Mn and Ni_3Fe), however, the kinetics of domain growth are very sluggish, and domain sizes are limited to about 500°A (Calvayrac and Fayard 1973). In some alloys, for example in Cu_3Au (Ardley 1955), domains can give rise to considerable strengthening. Also, the nature of the domain structure can give important information about fault energies as discussed below.

The antiphase boundary energy in Ll_2 alloys has been calculated to be anisotropic, with the lowest energy on {001} planes, taking into account first nearest neighbor (NN) interactions only (Flinn 1960). Accordingly, there is a driving force for an APB to lie on cube planes in these alloys, leading to important consequences with regard to yielding and strain hardening behavior. When this occurs, the electron microscope image of APB's shows a maze pattern (as in Cu_3Au and Cu_3Pt) rather than the "swirl" pattern that is associated with superlattices possessing isotropic domain networks (Ni_3Fe, Ni_3Mn, Fe_3Al). The morphology of an APB in Cu_3Au can be changed from a maze to a swirl pattern by adding 5 at% Ni (Yodogawa et al. 1980); this is perhaps due to a reduction in the electron/atom ratio and, hence, in the relative phase stability of Ll_2 versus long-period superlattices in which periodic {001} APBs are characteristic. Recently, swirl pattern APDs have been noted in rapidly quenched Ni_3Al-X alloys in which Ni_3Al-type compounds are formed (Inoue et al. 1983) as well as in binary Ni_3Al (Liu and Koch 1982); however, after short annealing treatments, these swirl patterns change to maze patterns and then quickly grow to large sizes (unpublished material, C. T. Liu, Oak Ridge National Laboratory, 1983).

In Ll_0-type alloys, domains are in the shape of plates in contact with each other on {110} planes. Detailed studies of the role of such APDs in plastic deformation of Cu-Au alloys have been reported in the Soviet Union by Grinberg and co-workers (1976).

The slip vector in B2-type superlattices varies from one alloy to another (Table 1) depending on factors such as APB energy, atom ratios,

atomic size ratios, and elastic energies of dislocations (Marcinkowski 1974). As in bcc metals, <111> is usually the slip vector, and slip occurs on planes of type {110}, {112}, and {123}; however, several B2 superlattices display <100> slip. In Ll_2 superlattices, on the other hand, the slip plane may change with temperature, as in Ni_3Al, which deforms on {111} planes at low temperatures and on {100} planes at high temperatures (Thornton et al. 1970). Cross slip from {111} to {100} is believed responsible for an anomalous increase in strain hardening rate of Cu_3Au with increasing temperature (Mikkola and Cohen 1966, Davies and Stoloff 1965, Duramoto and Pope 1976). The slip vector, however, is <110> at all test temperatures, but unit <110> dislocations probably dissociate into 1/6 a_o <112> partials.

Departures from Stoichiometry

Departures from perfect order cause strengthening through means not directly connected with the APB. Deviations in stoichiometry from the ideal AB or A_3B composition often lead to strengthening at low test temperatures, and, for this reason, slowly cooled alloys of the Fe-Co, Ni-Al, Ni-Ga, Mg-Cd, or Cu-Au systems reveal minima in room-temperature hardness at stoichiometric compositions. Hardness data obtained at 77°K and room temperature for compositions near stoichiometric Ni_3Ga and Ni_3Al are shown in Figure 3. Note the more rapid hardening with excess of the minority element. In systems with a very high ordering energy, the hardening at nonstoichiometric compositions might arise from lattice defects that are required to maintain the number of electrons per unit cell at a constant value required for phase stability (Guard and Westbrook 1959). In such cases, the vacancies should enhance plastic flow at high temperature, when the defects are mobile. Such behavior was reported for Ni_3Al by Guard and Westbrook (1959), who showed decreased flow stresses at 800°C in alloys containing an excess of either Al or Ni. However, Noguchi and co-workers (1981) have demonstrated significant hardening at elevated temperatures in aluminum-rich Ni_3Al (Figure 4) and in gallium-rich Ni_3Ga. Solute-induced hardening was attributed to changes in probability of cross slip from {111} to {100} plane with composition. Moreover, Aoki and Izumi (1975) showed that off-stoichiometric Ni_3Al does not contain excess vacancies. It is clear that lattice defects as a function of stoichiometry are an important research subject that remains to be addressed adequately.

Changes in stoichiometry influence not only the yield strength but also the dislocation substructure and fracture behavior. For example, unit dislocations are responsible for plastic deformation in hypo-stoichiometric Fe_3Al whereas paired dislocations are found for Fe-31 at% Al (Ehlers and Mendiratta 1982). Further, hypo-stoichiometric Ni_3Al and Fe_3Al are more ductile than hyper-stoichiometric compositions.

Yielding

Ordering exerts a significant influence on initial plastic deformation as well as on strain hardening of many single crystals. Initial yielding

16
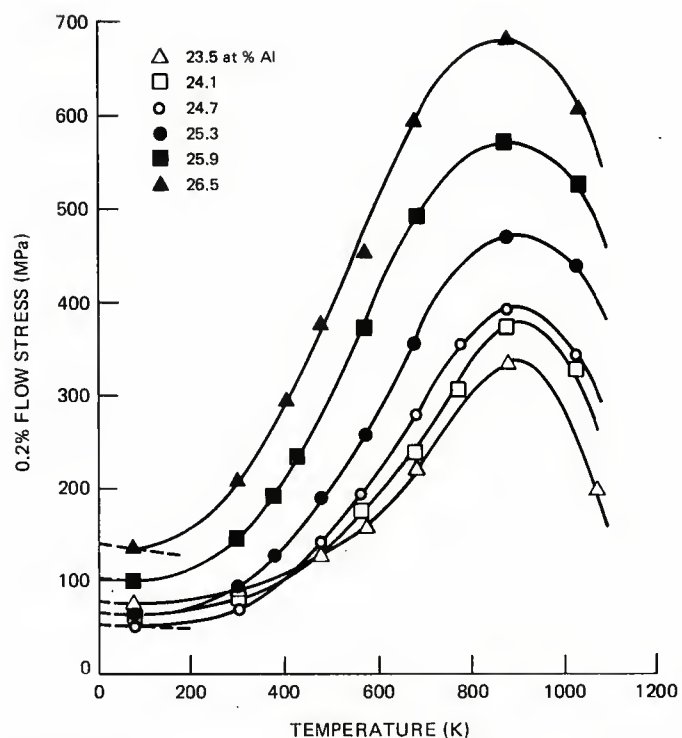
FIGURE 3 The effect of deviations from stoichiometry on the flow stress of Ni₃Al and Ni₃Ga at 77°K and room temperature (Noguchi et al. 1981).
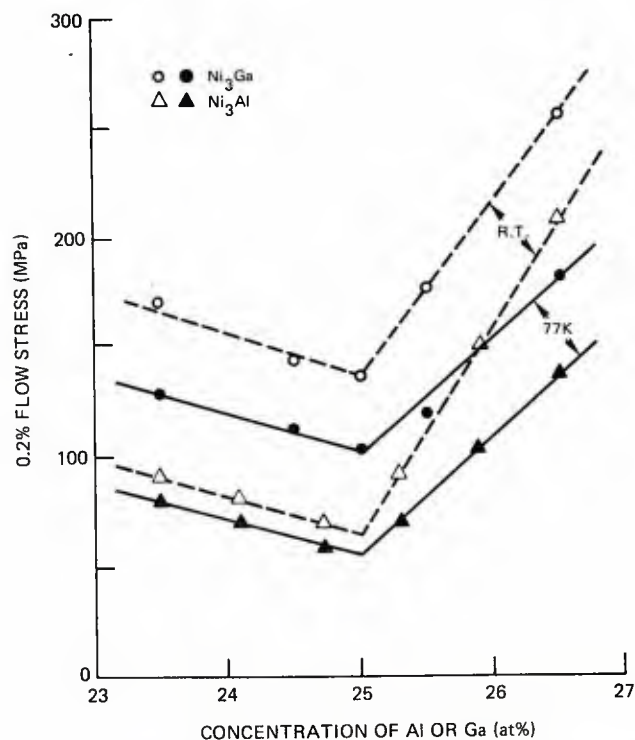
FIGURE 4 Effect of composition on the temperature dependence of yielding of binary Ni₃Al alloys (Noguchi et al. 1981).

generally occurs at a much lower stress in the ordered condition, but the more rapid strain hardening of the ordered condition causes the ultimate strength to exceed that of disordered materials. The interaction of unit dislocations with short-range-ordered regions produced by typical "disordering" treatments (quenching from above T_c) gives rise to a higher initial flow stress than for fully ordered material in which superlattice dislocations interact with large APD. A similar behavior is noted in many, but by no means all, superlattices. For example, ordering increases the yield strength of Ni_3Mn because of sluggish domain growth in that alloy (Johnston et al. 1965).

Strength (and ductility) data for representative aluminides appear in Table 3. Note that strengths are generally not very high at room temperature. In the case of NiAl, the yield stress is very sensitive to strain rate and composition, especially below 800°C (Pascoe and Newey 1971). One of the many striking features of the plastic deformation of most ordered alloys, particularly a large number of those with the $L1_2$ structure (e.g., Ni_3Al, $(Fe,Ni,Co)_3V$, Ni_3Ge, Ni_3Si, Ni_3Ga, Zr_3Al), is an anomalous sharp rise in flow stress with increasing temperature, as was shown in Figure 4 for Ni_3Al. The flow stress peak occurs in single crystals as well as in polycrystals and its position with respect to temperature in Ni_3Al is a function of crystal orientation (Kuramoto and Pope 1978) and alloy content (Thornton et al. 1970). Alloying with zirconium and hafnium is especially effective in raising the high temperature strength of Ni_3Al; the yield strength of these alloys is reportedly higher at 850°C than those of all commercial superalloys (unpublished material by C. T. Liu and A. C. Schaffhauser, Oak Ridge National Laboratory, 1983). Also, an asymmetry between flow stresses measured in tension and in compression has been reported (Ezz et al. 1982). There is no anomalous behavior with increasing temperature in a few cases (e.g., Fe_3Ge) (Suzuki et al. 1980). Since most advanced superalloys and several aligned eutectic (composite) alloys contain large volume fractions of Ni_3Al, the yield and ultimate tensile strengths of these alloys often rise or remain nearly constant with increasing temperature to at least 700°C.

Increases in flow stress with temperature also have been noted in long range ordered alloys of other cubic or hexagonal crystal structures. There is undoubtedly more than one mechanism responsible for this behavior since the peak strength is sometimes associated with the order-disorder temperature T_c or with the temperature of a transition from one ordered structure to another (e.g., Fe_3Al); in other cases, it bears no apparent relation to a transformation (e.g., Ni_3Al, β CuZn, and Ni_3Ge). A continuous range of behavior between anomalous and regular systems can be produced by alloying (e.g., by alloying Ni_3Ge with Fe_3Ge) (Suzuki et al. 1980). The addition of iron to Ni_3Ge causes the flow stress peak to disappear at an iron content of about 28 at%. Suzuki and co-workers (1980) have suggested that three factors control such behavior: APB and stacking fault energy on {111} and APB energy on {100} planes. A high anisotropy of APB energy between {100} and {111} planes is believed responsible for the strength anomaly in $L1_2$ alloys (Pope and Ezz 1984). This anisotropy leads to cross slip of superpartials onto {100} planes to minimize APB energy (Figure 5) (Kear and Wilsdorf 1962), thereby creating obstacles to further plastic flow. The obstacle density increases with increasing likelihood of

TABLE 3 Aluminide Mechanical Properties

Alloy at%	Condition	g.s. (μm)	0.2%σ_y (MPa)	UTS (MPa)	ε_F (%)	Fracture Mode	Reference
25°C							
Fe-31Al	Cast extruded	---	---	---	5.6	TG	Ehlers and Mendiratta 1981
Fe-35Al	RSR	---	---	---	7	Cleavage	Chaterjee and Mendiratta 1981a
Fe-50Al	RSR	---	---	---	0	IG	Chaterjee and Mendiratta 1981b
Ni-24Al+0.02B	Wrought[a]	30	300	1300	54	Dimples	Liu and Koch 1982
Ni3Al+1.5Hf+B	Wrought[a]	30	460	1460	47	Dimples	Liu 1983
Ni-25Al	---	---	90	---	---	---	Wee et al. 1980
Ti-54.2Al	PM	25	---	488	0.1	Cleavage	Lipsitt et al. 1975
Ni-50Al	PM	100	220	---	0	Cleavage, IG	Schulson 1982
Ni3Al+1 at% B	Melt spun	---	690	---	---	TG	Taub et al. 1984
Ni-25Al	Poly.	---	230	---	---	---	Taub et al. 1984
500°C							
Fe-35	RSR	---	---	---	---	Dimples	Chaterjee and Mendiratta 1981a
Fe-50	RSR	---	---	---	"High"	---	Chaterjee and Mendiratta 1981b
Ni-24Al+B	Wrought[a]	30	540	1100	42	Dimples	Liu and Koch 1982
Ni3Al+1.5Hf+B	Wrought[a]	30	700	1270	36	Dimples	Liu 1983
Fe-40Al	Wrought[a]	100	---	500	30(RA)	---	Sainfort 1967
Fe-30.9Al-15.2	RSR/PM	---	813	992	5.4	---	Ray et al. 1983
Fe-36.4Al 2.3Mo-2.3V 4B	RSR/PM	---	947	1118	2.5	---	Ray et al. 1983
Fe-28Al-12B	RSR/PM	2	813	967	7.6	---	Ray et al. 1983

[a]Recrystallized
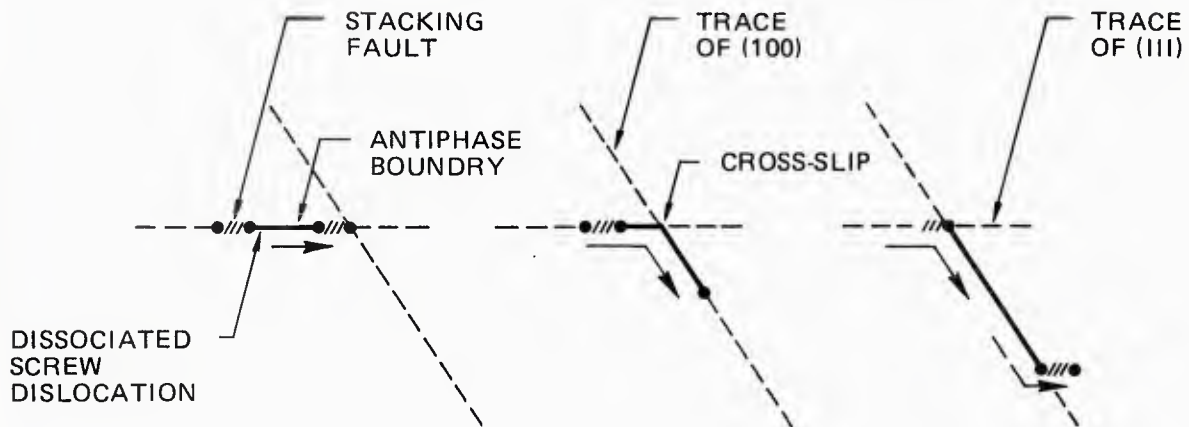
FIGURE 5 Cross slip of leading dissociated screw dislocations from (111) to
(001), favored by lower APB energy on (001) (Kear and Wilsdorf 1962).

cross slip onto {100}, whether through raising temperature or testing
crystals favorably created for cross slip.

In the case of alloys such as FeCo-2% V, where the flow stress peak
occurs at the order-disorder transition temperature, and Fe_3Al, where the
flow stress peak occurs just under the temperature for a transition between
two ordered structures, the anomaly has been attributed to a transition from
plastic deformation by superlattice dislocations at temperatures below that
of the peak to deformation by unit dislocations at temperatures above that
of the peak (Stoloff and Davies 1964a). However, this mechanism cannot
apply to Fe_3Al in which the aluminum content is less than 25 at%, since
only unit dislocations have been observed in the DO_3 condition. Fujita et
al. (1983) have suggested that changes in the anisotropy between {010} and
{111} APB energies produced by alloying can alter the mechanism of yielding
in Cu_3Au. Other mechanisms for the flow stress peak are discussed in the
literature (Hanada et al. 1981, Van der Wegen et al. 1982), but it is clear
that additional work on identifying dislocation configurations in the
temperature range of the observed flow stress peaks is needed.

Strain Hardening

Long-range-ordered alloys usually exhibit high strain-hardening rates compared to their disordered counterparts. For Ll_2 superlattices, the strain-hardening rate can double with order at temperatures near 298°K whereas lesser increments in rate are noted in cubic B2 or DO_3 systems (e.g., FeCo-2% V and Fe_3Al); for hcp DO_{19} Mg_3Cd, there is no change in strain-hardening rate with order at 298°K (Stoloff and Davies 1966). The role of superlattice dislocations in work hardening is controversial. For example, one model is based on the formation of "super-jogs" by the intersection of superlattice dislocations and the difficulty of dragging these super-jogs during continuing plastic deformation (Vidoz and Brown 1962). Since these super-jogs usually are not seen in thin foils of deformed alloys, an alternative mechanism based on the cross slip of superpartial onto {100} planes (as first suggested by Kear and Wilsdorf 1962) (Figure 5) also has been proposed to account for rapid hardening (Stoloff and Davies 1966). Experimental data obtained to date, including the observation that the rate of work hardening in ordered Cu_3Au increases with temperature, generally favor the latter model; this point has been described in more detail in a recent paper by Pope and Ezz (1984).

High strain hardening rates induced by long range order may permit attainment of very high strengths through cold working operation or thermal-mechanical treatments. Wear-resistance also should be enhanced by rapid strain hardening, permitting possible replacement of cobalt-base alloys for such applications.

Fracture

Polycrystalline ordered alloys often are brittle when tested in tension although considerable plasticity may be displayed by single crystals or by polycrystals tested in compression. In the Fe-Co system, brittleness and ordering fall in the same composition range, 35 to 65 percent cobalt (Stoloff and Davies 1966). The addition of a few percent of vanadium or chromium increases ductility of alloys tested in the quenched condition, perhaps as a result of the slowing of ordering kinetics (rapid quenching of binary FeCo always leaves some residual order).

Recently, small additions of molybdenum, tungsten, tantalum, niobium, carbon, and nickel also have been shown to improve workability (ductility) of equiatomic Fe-Co alloys (Kawahara 1983). Each of the elements that improved ductility were capable of forming Co_3X compounds by diffusion, leading Kawahara to suggest that disruption of B2-type order occurs in the vicinity of Co_3X zones. He also noted that there is no correlation between the reactivity of solutes with interstitials, such as C, N, and O, and ductility.

A direct relationship between ductility and the degree of long-range order has been demonstrated in FeCo-2% V (Stoloff and Davies 1966). Varying composition in binary alloys or adding ternary solutes influences the ductility of other alloys with the B2 structure. Solute effects may occur, in some cases, by interaction of solute elements with interstitial impurities or by affecting slip character. For example, nickel promotes wavy slip in β-CuZn and reduces brittleness, whereas manganese suppresses

wavy slip and raises the ductile-to-brittle transition temperature (Shea and Stoloff 1974). In the Fe-Al system, a sharply reduced ductility is observed as the aluminum content approaches 25 at% (Figure 6) (Marcinkowski et al. 1975); alloys with 25 to 50 at% Al have usually been reported to be completely brittle at room temperature when processed by conventional ingot techniques. However, recent work has shown that the ductility of alloys with aluminum contents in the range 31 to 35 at% can be as much as 5 to 7 percent at room temperature (Chaterjee and Mendiratta 1981a, Ehlers and Mendiratta 1981). In addition, Fe-20 at% Al 5%Si exhibits a small amount of plasticity at room temperature; failure was by transgranular cleavage, with a transition to intergranular cavitation at higher test temperatures (Ehlers and Mendiratta 1982). Ti_3Al and $TiAl$ are brittle below about 600°C, as shown in Figure 7 for $TiAl$ (Lipsitt et al. 1975), but some success in improving ductility through additions of germanium and zirconium have been reported.

Only in the case of hcp Mg_3Cd has long-range order been reported to increase ductility (Stoloff and Davies 1964b). In this alloy, slip occurs on more slip systems in the ordered than in the disordered state whereas in all other alloys studied to date, ordering either reduces the number of available slip systems or restricts cross slip of screw dislocations from one slip plane to another. For this reason, the brittleness of many polycrystalline ordered alloys has been attributed to a lack of sufficient slip systems to provide compatibility of deformation at grain boundaries under arbitrary states of strain. In the case of AgMg and the aluminides, the segregation of impurities to grain boundaries has been suggested to be the predominant factor (Westbrook and Wood 1963). However, recent work on high-purity NiAl and Ni_3Al has shown that impurity segregation in these alloys is minimal (private communication with E. R. Schulson, Dartmouth University, Hanover, New Hampshire, 1983); yet, they remain brittle.

Considerable effort is being devoted to improving the ductility of several aluminides (FeAl, Fe_3Al, NiAl, Ni_3Al) through such diverse techniques as grain refinement through thermal-mechanical treatment, microalloying with boron, and various rapid solidification techniques. A particularly promising development is the demonstration of high ductility of Ni_3Al doped with small quantities of boron (Aoki and Izumi 1979, Liu and Koch 1982). Boron segregates preferentially to grain boundaries (Liu et al. 1983). Unfortunately, the beneficial effect of boron seems to be lost at 25 at% Al (Liu and Koch 1982); Taub et al. (1984) report that some ductility can be achieved in rapidly solidified Ni-25 at% Al with 1%B. Schulson and Barker (1983) recently reported that an elongation of more than 40 percent can be achieved in Ni-49 at% Al at 400°C when the grain size is reduced to less than 20μm (Figure 8), while the ductility at 25°C by this treatment was 3 to 5 percent. (A summary of ductility data for aluminides at 25°C and 500°C is presented in Table 3.)

There have been several reports in the literature of a beneficial effect of partial recrystallization on ductility of B2-type alloys. For example, fully ordered FeCo-2%V exhibits about 5 percent elongation or reduction in area at grain sizes in the range 12 to 100μm. When partially recrystallized, however, the ductility of ordered FeCo-2%V increases to about 20 percent (Stoloff and Dillamore 1970). Recently, Schulson (1982) has reported a small increase in ductility by partially recrystallizing
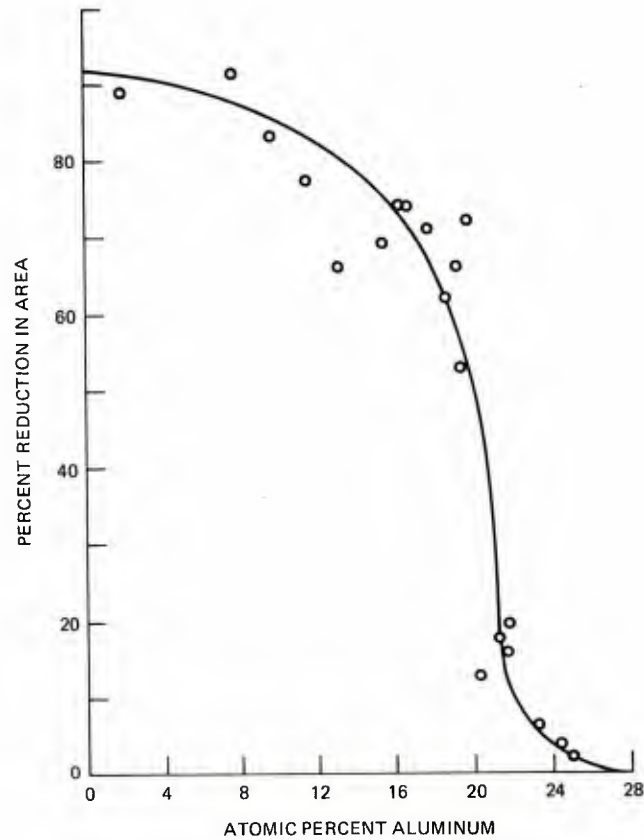
FIGURE 6 Ductility of Fe-Al alloys slowly cooled to 477°K and fractured in tension at that temperature (Marcinkowski et al. 1975).
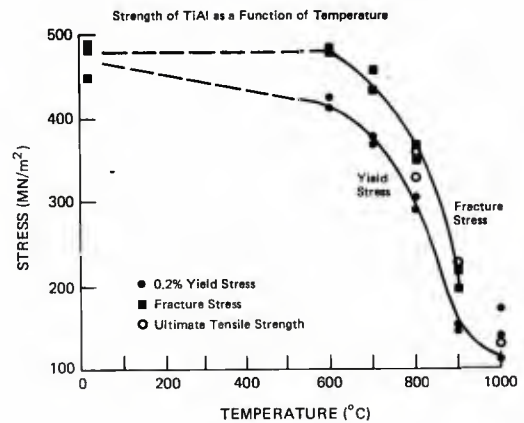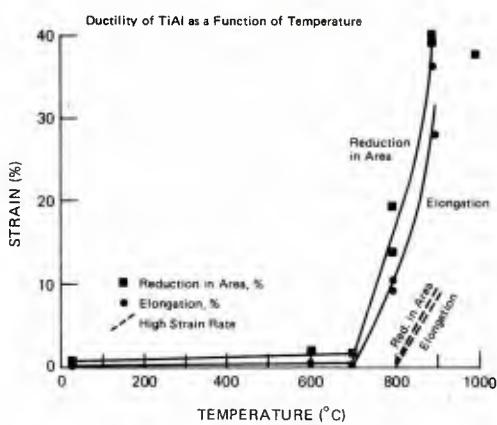
FIGURE 7 Effect of temperature on tensile properties of TiAl (Lipsitt et al. 1975).
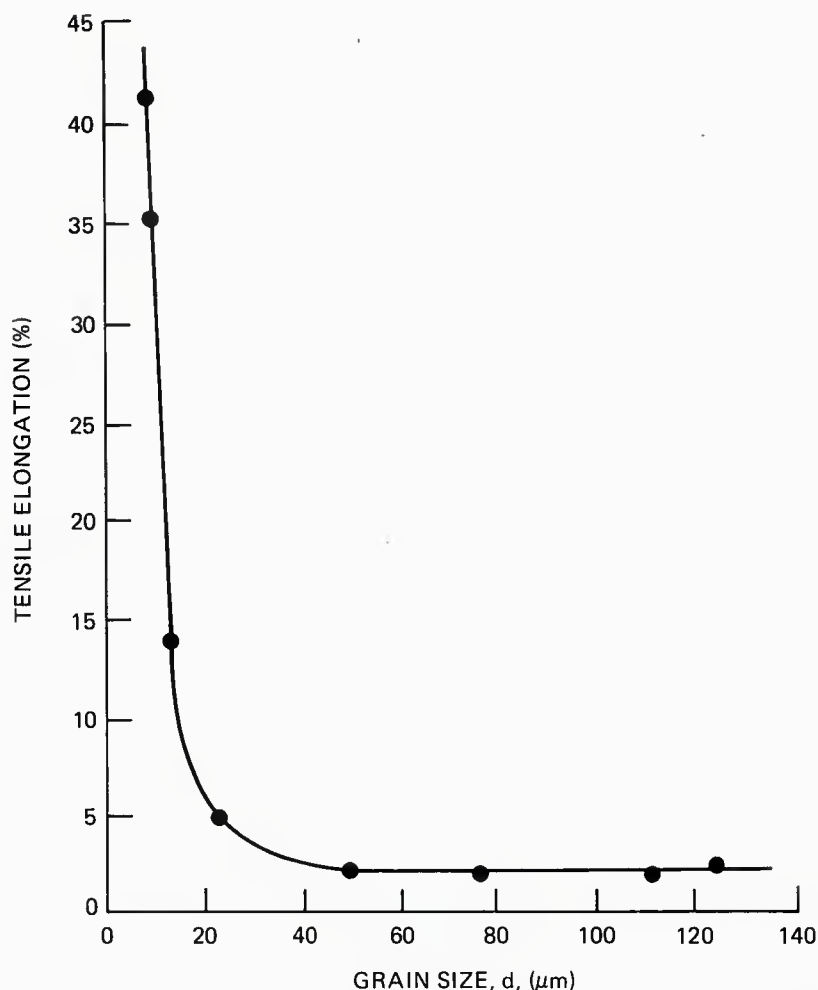
FIGURE 8 Influence of grain size on tensile ductility of NiAl at 673°K; strain rate = 10^{-4} s^{-1} (Schulson and Barker 1983).

NiAl. Ductility improvements can also be achieved through control of the microstructure by rapid solidification techniques such as melt spinning.

It has been shown by Inoue and co-workers (1983) that melt-spun Ll$_2$ compounds of type Ni-Al-X (X=Cr, Mn, Fe, Co or Si) are both strong and ductile whereas their conventionally solidified counterparts are extremely brittle. The most effective strengtheners were chromium and silicon, which produced yield strengths of 490 and 590 Mpa at compositions of Ni$_{67.5}$Al$_{20}$Cr$_{12.5}$ and Ni$_{78}$Al$_{10}$Si$_{12}$, respectively. Silicon also has been reported to be an effective strengthener in conventionally prepared Ni$_3$Al (Guard and Westbrook 1959). However, the high strength of the melt-spun alloys decreases significantly after subsequent annealing (e.g., after annealing at 1000°C for 1 hr), and the strength loss is accompanied by a drastic drop in ductility and a change from transgranular to intergranular cracking (Inoue et al. 1983). The change was attributed to an increased degree of long-range order and segregation of solutes to grain boundaries. Koch and co-workers (1982) also have been able to produce ductile Ni$_3$Al

containing small additions of boron using an arc hammer apparatus, but the quench rates could not exceed a critical value. No ductility was achieved without boron. Taub and co-workers (1984), on the other hand, have not only reported that boron has a beneficial effect on the ductility of melt-spun Ni_3Al, but have, further, reported that powder-processed Ni_3Al with 1% B also demonstrates appreciable ductility These apparently conflicting reports suggest again that small differences in composition may play a significant role in determining both strength and ductility.

RSR processing via the PM route also has been employed to produce intermetallic compounds with improved ductility. For example, off-stoichiometric FeAl (35% Al) (Chaterjee and Mendiratta 1981a) with a room temperature ductility of 7 percent has been produced by the RSR process. An RSR alloy containing 50 at% Al, however, was brittle at temperatures up to 400°C, but high ductilities were observed at 500°C (Chaterjee and Mendiratta 1981b). For Fe-35 at% Al, fracture was by transgranular cleavage at room temperature while intergranular fracture occurred at 600°C. FeAl (50 at% Al) displayed intergranular failure at low temperatures (Chaterjee and Mendiratta 1981b). Fe_3Al and FeAl containing sufficient quantities of boron to produce borides also have been prepared by RSR (Slaughter and Das 1980) and by melt spinning followed by pulverization and powder processing (Ray et al. 1983), but relatively little properties data have been reported in the open literature. A summary of all rapid solidification processing efforts reported to date appears in Table 4.

TABLE 4   Rapid Solidification of Aluminides

Alloys	Method	Remarks	Reference
Ni-Al-X	Melt spin	Ductile at 25°C, unstable at 1000°C	Inoue et al. 1983
Ni_3Al-B	Arc hammer	Ductile	Liu and Koch 1982
FeAl-borides	Melt spin & PM	Brittle to 540°C	Ray et al. 1983
Fe-35 at% Al	RSR	TG at 25°C, IG at 600°C	Chaterjee and Mendiratta 1982a
Fe-50 at% Al	RSR	Brittle to 400°C, IG	Chaterjee and Mendiratta 1982b
Ni_3Al-B	Melt spin	Ductility varies with B	Liu and Koch 1982
Fe_3Al-TiB_2	RSR	Finely dispersed borides	Slaughter and Das 1980

The benefits of rapid solidification on the ductility of aluminides at low temperatures have been suggested to be the following:

1.   Elimination of macrosegregation and grain boundary segregation (both RSR and melt spinning).

2.   Production of very fine grained material ($\sim$ 3μm grain size by melt spinning, 1-2μm by RSR).

3.   Reduction in the degree of order as an interim step during processing (melt spinning).

However, the investigations reported above also have demonstrated certain disadvantages with respect to high-temperature mechanical properties:

1.   Loss of strength and ductility of melt-spun Ni_3Al-type alloys after annealing.

2.   Elevated temperature intergranular fracture in RSR-processed Fe-Al alloys (Chaterjee and Mendiratta 1982a, 1982b).

3.   Inadequate stress rupture strength of melt-spun and PM-processed Fe-Al-B alloys at temperatures above 537°C (1000°F) (Ray et al. 1983).

A further disadvantage of the melt spinning process is the restriction of product to thin sections (e.g., 0.1 mm thickness), and the sensitivity of the ribbons to surface imperfections produced upon solidification. However, these disadvantages can be eliminated if the melt-spun foils are pulverized and then processed by PM techniques, as has been done with Fe-Al alloys containing borides (Ray et al. 1983). This material is brittle at room temperature and, when inclusions are present, exhibits poor low cycle fatigue resistance at 650°C (unpublished material by A. K. Kuruvilla and N. S. Stoloff, Rensselaer Polytechnic Institute, Troy, New York, 1983).

Liu and co-workers (Liu 1973, Liu 1979, and Liu and Inoue 1979) have utilized a combination of macro and micro alloying principles to achieve ductility in ordered alloys based on tetragonal Ni_3V and hexagonal Co_3V without resorting to rapid solidification. The unmodified alloys are very brittle in the ordered state. Work on ternary $(Co,Ni)_3V$ alloys showed that considerable ductility could be achieved by control of the ordered structure through alloying to control the electron/atom (e/a) ratio (Liu 1973), as first suggested by Beck (1969). In particular, replacing cobalt in Co_3V with both iron and nickel produced an Ll_2 superlattice. Several alloys of varying cobalt, iron and nickel content have been shown to be ductile at room temperature and to exhibit strengths superior to those of conventional single-phase alloys (e.g., austenitic stainless steels, Hastelloy X) at temperatures of 600 or 800°C (Figure 9) (unpublished material by C. T. Liu, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983). Ductility problems at elevated temperatures have been alleviated through addition of small amounts of reactive solutes such as titanium and rare earths to the alloys. The effect of these is to suppress intergranular cracking. Figure 9 shows yield strength data for an advanced LRO alloy as well as for alloys based on Ni_3Al. Both the aluminide alloys and the LRO alloys show a substantial strength increase between room temperature and elevated temperatures, as is usually noted with Ll_2-type superlattices.

THE YIELD STRENGTH OF ORDERED INTERMETALLIC ALLOYS INCREASES WITH TEMPERATURE
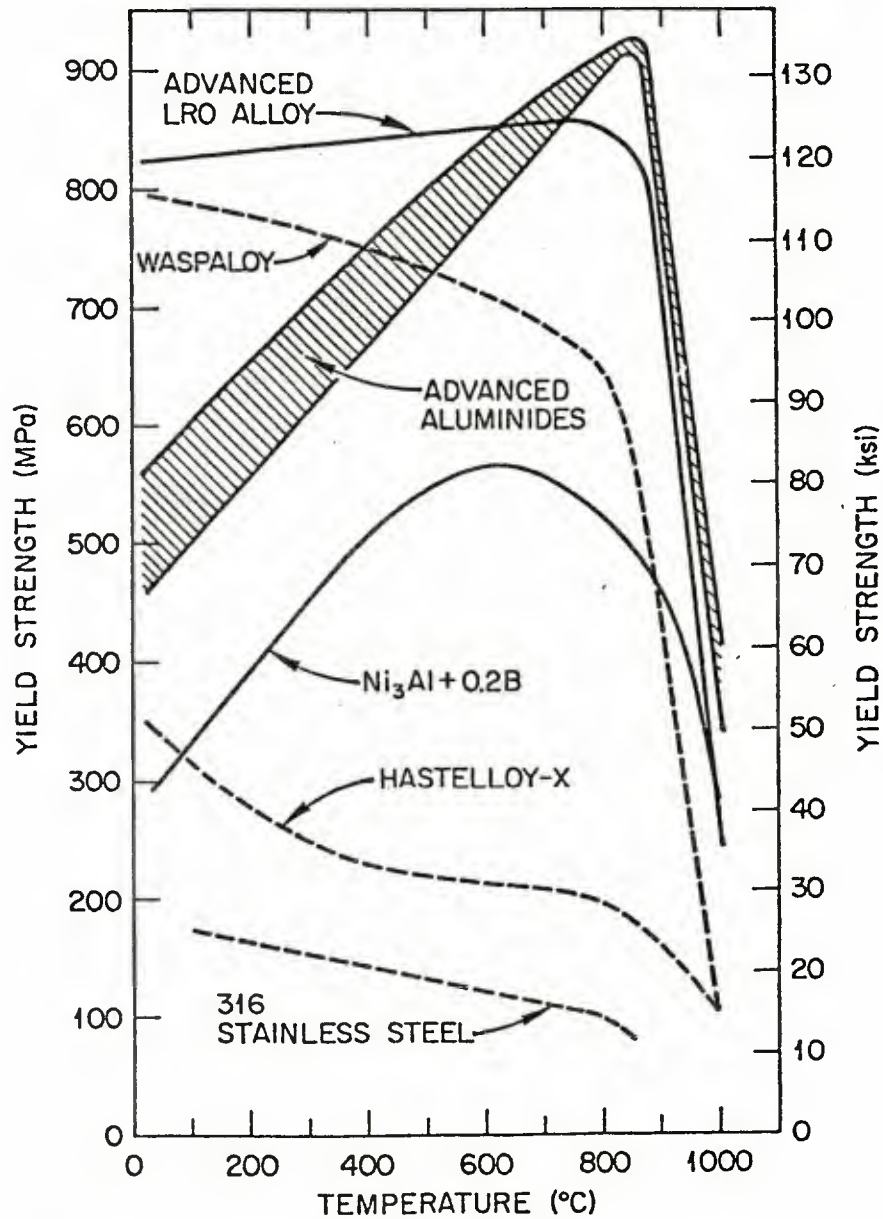
FIGURE 9 Comparison of the yield strengths of advanced LRO alloy and nickel aluminides with commercial structural alloys (unpublished material by C. T. Liu, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983).

Creep

Diffusion-controlled phenomena such as recovery, recrystallization, creep, and oxidation are suppressed by long-range order. The improvement in steady-state creep resistance with increasing order is manifested by an increase in the activation enthalpy, ΔH (Lawley et al. 1960, Hren and Sherby 1965). The steady-state creep rate of alloys often can be expressed as:

$$\dot{\varepsilon} = A(\frac{\sigma}{G})^{ne}\, e^{-\Delta H/RT}$$

where A is a constant, T is absolute temperature, R is the gas constant, σ is the applied stress, G is the shear modulus, and n is a constant of the order of 4-6. Tracer experiments to determine activation energies for diffusion in ordered systems have provided values in close agreement with activation energies for creep. Since self-diffusion depends on vacancy interchange with atoms, the activation enthalpy is the sum of the enthalpies of formation and migration for vacancies. Both the enthalpies of formation and migration increase with the formation of long-range order, resulting in higher activation enthalpies for diffusion and for creep, and, therefore, lower creep rates. In the case of LRO alloys, however, formation of long range order causes only a small increase in ΔH, even though the creep rate is decreased by two orders of magnitude (Liu 1984). The stress exponent, n, has been shown to be highly stress-dependent in AgMg (Lexcellent et al. 1982) and disordered FeCo-2% V (Delobelle et al. 1979) and somewhat less stress dependent in ordered TiAl + 10% Nb (Mendiratta and Lipsitt 1980).

Creep resistance of unalloyed NiAl (Vandervoort et al. 1966, Strutt and Dodd 1969) and Ni_3Al (G. Leverant and D. Duhl as reported by Strutt and Dodd 1969, and Davies and Johnston 1970) tends to be poor relative to that of commercial high temperature alloys. However, alloying of boron-modified Ni_3Al with hafnium and zirconium provides creep resistance comparable to or better than that of Waspaloy, a nickel-base alloy widely used in gas turbines (unpublished material by C. T. Liu and A. C. Schaffhauser, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983). Advanced LRO alloys, in which aluminum replaces vanadium, also display good creep resistance, although not quite as high as that of Ni_3Al+B (Table 5). These results, which were obtained at a very early stage of development of both classes of alloys, suggest the desirability of further intensive research on these systems.

Limited stress rupture data for Fe-20.8w%Al-4.1%B (30.9 at% Al-15.2%B) show that at 538°C (1000°F) the 100 hour specific creep strength is comparable to that of A-286, an Fe-Ni superalloy (Ray et al. 1983). However, with increasing temperature the stress rupture strength of the very fine grained rapidly solidified Fe-Al-B alloy drops at a faster rate than for the conventionally processed, coarser grained A-286. Control of grain size is expected to be a problem in providing balanced creep and tensile properties of all rapidly solidified alloys.

Experiments on the slow strain rate behavior of Fe-39.8 at% Al (B2 structure) produced by powder metallurgy indicate that extrusion temperature can affect high temperature deformation mechanisms. Grain size refinement

TABLE 5 Comparison of Creep Properties of Advanced LRO Alloys and Nickel Aluminides with Commercial Alloys

Alloys	Steady–State Creep Rate (10^{-6}/h)	Rupture Life or Test Time (h)
At 20,000 psi, 760°C		
Boron–doped Ni_3Al	34	500
Advanced Ni_3Al aluminides	3	600[a]
Advanced LRO alloys (Fe, Ni)$_3$(V,Al)	7	500[a]
Type 316 stainless steel	8,500	65
Hastelloy X	1,300	200
At 40,000 psi, 760°C		
Advanced Ni_3Al aluminides	20	600[a]
Advanced LRO alloys (Fe,Ni)$_3$(V,Al)	30	600[a]
At 94,000 psi, 760°C		
MAR–M–246	133	1000

[a]The test was stopped (without rupture) at the time indicated.
SOURCE: Private communication with C. T. Liu, Oak Ridge National Laboratory, 1983.

to about 10µm produced effective strengthening to at least 0.75 of the melting temperature (Whittenberger 1983).

Fatigue

The suppression of cross slip or reduction in number of available slip systems with long-range order that occurs in most alloys suggests a diminished probability of crack nucleation under cyclic loading. In the few systems for which room-temperature fatigue data have been published (e.g., FeCo-2%V and Ni_3Mn, ordering does, indeed, lead to an increase in high-cycle (stress-controlled) fatigue life (Boettner et al. 1966). The most detailed account of fatigue resistance in an ordered alloy is that of Williams and Smith (1966), who reported on the high-cycle behavior of brass at 25°C. The marked elastic anisotropy in this alloy produces severe stress concentrations at grain boundaries, leading to intercrystalline crack initiation. Williams and Smith (1966) also showed that the fatigue limit of this alloy is reduced when the sample is tested in a 3 percent aqueous solution of NaCl. Crack propagation data are not available in the literature for ordered alloys although recent work has shown that the crack growth resistance of an (FeNi)$_3$V alloy is superior to that of conventional alloys at both 25°C, and 600°C (unpublished material by A. K. Kuruvilla and

N. S. Stoloff, Rensselaer Polytechnic Institute, Troy, New York, 1983)
(Figure 10). Data on high-temperature fatigue resistance are few, with work
reported for only four systems: TiAl (Sastry and Lipsitt 1977a), Ti$_3$Al
(Sastry and Lipsitt 1977b), (CoNi)$_3$V (Ashok et al. 1983), and Cu$_3$Au
(Gittins 1968). In each case there is a tendency towards increased
intergranular crack propagation as temperature increases. In the
cobalt-base alloys this tendency can be reduced by doping with Ti (Ashok
et al. 1983).

There are even fewer data available on low-cycle fatigue (LCF) of
ordered alloys. LCF resistance of Cu$_3$Au is little affected by long-range
order although fully ordered crystals cyclically harden much more rapidly
than disordered crystals (Chien and Starke 1975). A cyclic strain-hardening
exponent, n=0.36, has been reported, but this value is higher than that
observed for most materials. Ordering has little effect on the fracture
mode of Cu$_3$Au; ductile fracture was observed under all conditions.
Limited LCF data at 650°C for Fe-20.8 W%Al-4.1%B have recently been reported
(Ray et al. 1983). Comparisons with several other engineering alloys,
including an (Fe,Ni)$_3$V alloy (LRO-49) are shown in Figure 11.

Environmental Cracking

The previously described changes in slip character caused by long-range
order, most notably reduced cross slip in alloys with high anisotropy in APB
energy, suggest that there should be a significant effect of LRO on
resistance to environmental cracking since increased susceptibility to
stress corrosion cracking of some austenitic steels deforming by planar
glide has been noted (Barnartt 1962) [although this association has been
disputed (Saxena and Dodd 1966)]. A change in crack path from intergranular
in low-Zn alpha brasses to transgranular in high-Zn alpha brasses also has
been linked to a change in slip character (Swann 1963). Nevertheless, few
studies of the influence of LRO on environmental cracking have been
reported. In the case of Hastelloy B, attempts to link LRO with increased
susceptibility to hydrogen embrittlement were inconclusive (Berkowitz and
Miller 1980) although LRO had been suggested to be the cause of
embrittlement (Asphahani 1977). Increased embrittlement (in the presence of
hydrogen) of FeCo-2%V and an (Fe,Ni)$_3$V alloy (LRO-42) when the alloys were
ordered has been demonstrated by means of tensile, delayed failure, and
fatigue tests (Kuruvilla et al. 1980). A possible explanation for an
enhanced susceptibility to hydrogen embrittlement due to ordering is the
possibility of the transport of hydrogen over long distances by superlattice
dislocations confined to the original slip planes. However, no marked
change in slip character with ordering has been noted by ordinary
metallographic observations in these alloys. Recently, hydrogen
embrittlement also has been noted in Ni$_3$Al+B tested in tension at room
temperature (unpublished material by A. K. Kuruvilla and N. S. Stoloff,
Rensselaer Polytechnic Institute, Troy, New York, 1983). The embrittlement
was shown to be reversible after an outgassing treatment at 200°C.

Wear Resistance

The pronounced effects of ordering on the mechanical and physical properties
of alloys suggest that wear resistance also might be influenced by
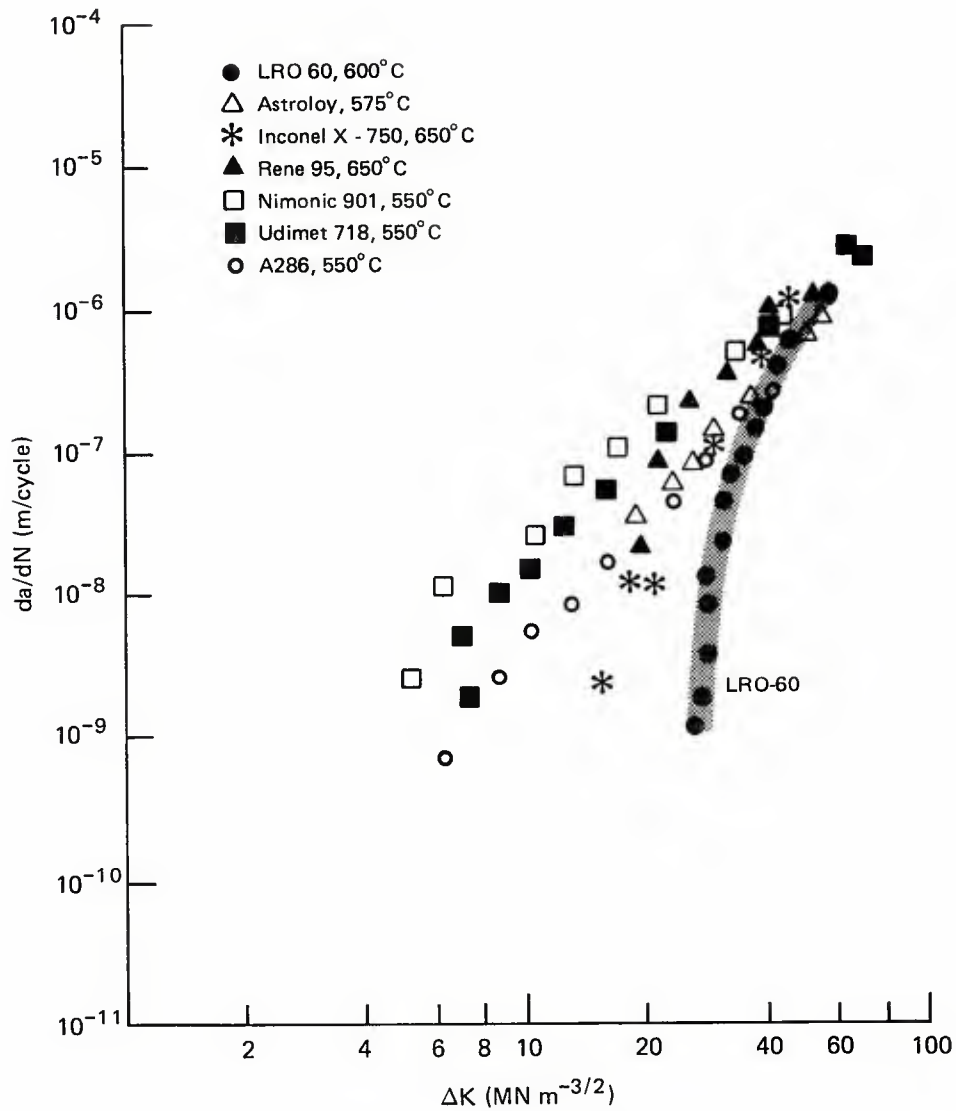
FIGURE 10 Comparison of crack growth data for LRO-60 (Fe-39.5w%Ni-22.4V-0.4Ti-0.04Ce) in high purity argon with other high-temperature alloys: Astroloy tested in high purity argon, R = 0.05, ν = 10 Hz; Rene 95 tested in high purity argon, R = 0.05, ν = 20 Hz (unpublished material by A. K. Kuruvilla and N. S. Stoloff, Rensselaer Polytechnic Institute, Troy, New York, 1983); Nimonic 901, Udimet 718, and A-286 tested in air at R = 0.1, ν = 40 Hz (Hoffelner and Speidel 1981).
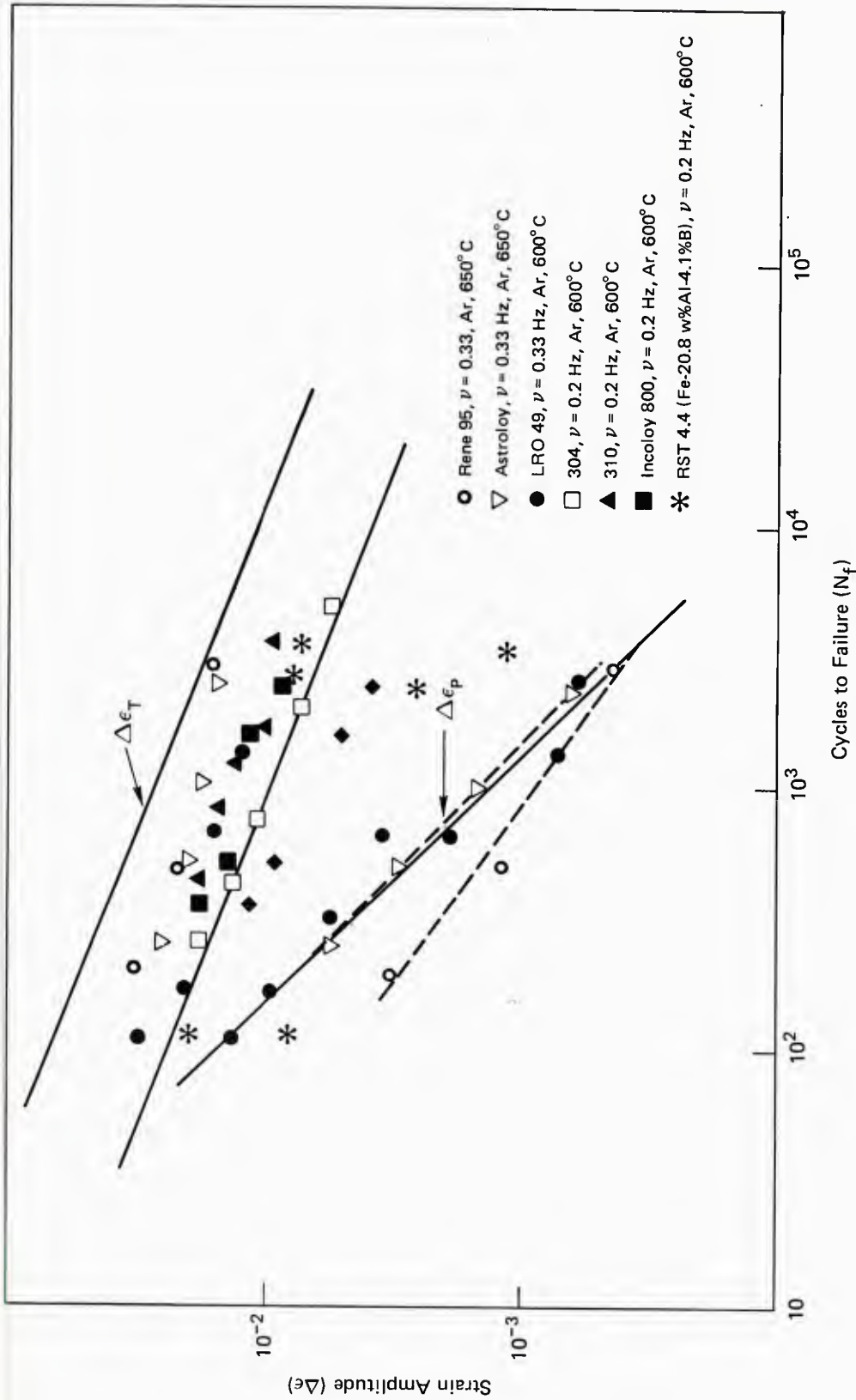
FIGURE 11 Low-cycle fatigue of ordered alloys compared to commercial alloys: Rene 95 ○ and Astroloy ▽ (unpublished material, S. V. Golwalkar, Rensselaer Polytechnic Institute); LRO 49 ● (unpublished material, A. K. Kuruvilla, Rensselaer Polytechnic Institute, 1983); 304 □, 310 ▲ and Incoloy 800 ■ (unpublished material, C. Zhi Ben, Rensselaer Polytechnic Institute, 1983); and RST 44 ✳ (Ray et al. 1983).

long-range order. It has been shown, for example, that the coefficient of adhesion is changed by long-range order (Bailey and Sikorski 1967). For Cu-Au and Pt-Co alloys, the coefficients are lower for the ordered conditions. The observed effects were related to order-induced changes in hardness. Similar observations have been made by Buckley (1965) for the frictional behavior of Cu-Au alloys in vacuum. Although little work has been done on the effects of long-range order on erosion resistance, work on Cu_3Au (Wright and Mikkola 1976) has shown that the finer slip in the ordered material enhances the erosion resistance.

CURRENT STRUCTURAL USES OF ORDERED ALLOYS

Ordered alloys currently are used as single-phase (or as the continuous phase of multiphase) alloys in relatively few structural applications. Aluminide coatings based on NiAl and CoAl have been applied to nickel and to cobalt-base airfoils in gas turbines for about 15 years. In some cases these coatings, which were applied by chemical means (e.g., pack cementation), have been superseded by overlay coatings based on solid solution alloys such as NiCrAlY, FeCrAlY, and CoCrAlY. Platinum coatings have been used by the General Electric Company to form aluminides on turbine blade surfaces.

Intermetallics as distributed phases constitute the most significant and unique feature of nickel-base superalloys. Conventionally cast and directionally solidified superalloys often contain 60 to 65 vol % Ni_3Al, in which substantial quantities of titanium, tantalum, niobium, and other elements are dissolved. Such alloys provide the best combination of strength and oxidation/corrosion resistance available for temperatures from about 760 to 1100°C. Many directionally solidified nickel-base eutectic alloys contain γ' particles to strengthen the γ matrix, and some are reinforced by intermetallic fibers (e.g., $\gamma'-\delta$ and $\gamma/\gamma'-\delta$ alloys in which $\delta=Ni_3Nb$ and Co-CoAl alloys in which CoAl is the continuous phase). Although directionally solidified eutectic alloys have not been commercially manufactured, some have been engine tested successfully under relatively short time conditions and may in the future be selected for turbine applications, especially if production costs can be reduced.

Zr_3Al was seriously considered as a fuel element sheath in Canada because of a combination of low neutron capture cross-section coupled with high strength and corrosion resistance comparable to that of Zircaloy 2 (Schulson 1974). However, development of this alloy ultimately was halted as a result of recognition of notch sensitivity and swelling upon irradiation.

CONCLUDING REMARKS

This chapter has shown that ordered alloys offer a number of unique properties that make them extremely attractive for structural use. Among them are a high specific modulus, especially at elevated temperatures, high strength at elevated temperatures, high strain-hardening rates, and low

self-diffusion rates with resulting low creep rates and high recrystallization temperatures. A major problem with most ordered alloys has been a tendency for low ductility; however, recent work performed in the United States and Japan has shown that there are a number of reasons for the brittleness of ordered alloys, and the reasons can be quite varied depending on the alloy system. Furthermore, it has been clearly demonstrated that once the reasons for the brittleness of a given alloy have been identified, the ductility can, in many cases, be dramatically improved. These improvements now make it possible to consider ordered alloys for a much greater range of structural uses.

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3

CURRENT RESEARCH ON ORDERED ALLOYS

U.S. EFFORTS

Research efforts in the United States to develop ordered alloys for
structural applications are currently being sponsored by several government
agencies (i.e., ONR, NSF, DOE, NASA, and Air Force Wright Aeronautical
Laboratories). A compilation of research programs, sources of support, and
principal investigators appears in Table 6. Most of these are on-going
programs, although one or more may have recently terminated. Other
companies that have been involved in research on titanium aluminides are
TRW, Inc., Rockwell International Corporation, and Battelle-Columbus
Laboratories. Noteworthy by its low level of support is the National
Science Foundation, which is currently funding only two basic research
efforts on aluminides, on the flow stress peak in Ni_3Al, at the University
of Pennsylvania, and some work on NiAl as part of a program at Case Western
Reserve University to evaluate the effects of surface coatings on ductility
of refractory metals. With the exception of some very innovative
applications of alloying principles to produce fcc ordered alloys at Oak
Ridge National Laboratory, there is no current effort to broaden our
fundamental knowledge of structure, ordering kinetics, and mechanisms of
plastic deformation in ordered alloys. Consequently, the current, largely
applied, research programs are utilizing basic research results of the past
or those of overseas workers, thereby jeopardizing the leadership position
of the United States in this field. The significant number of universities
listed in Table 6 does not represent a completely accurate picture of the
apportionment of research effort, since many of these programs are small.
Also, several groups at universities that previously have had significant
programs on basic research on structure and properties of ordered alloys no
longer are active in this field (e.g., Iowa State University-Ames
Laboratory, the University of Maryland, and the University of California-
Los Angeles).

Other research programs on using ordered alloys as strengthening phases
in multiphase eutectic composites have been carried out in the United States
at United Technologies Research Center, General Electric Company, and
Rensselaer Polytechnic Institute, largely under DOD sponsorship. Reviews of
the status of such programs recently have been published (McLean 1982,
Stoloff 1979).

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TABLE 6 Compilation of Research Efforts on Ordered Alloys in the United States

Laboratory	Source of Funding	System Studied	Principal Investigators
NASA-Lewis	NASA	FeAl	D. Whittenberger
AFWAL	AF	$Fe_3Al, TiAl, Ti_3Al$	H. Lipsitt
Systems Res. Lab	AF	$Fe_3Al, FeAl, Fe_3Si$	M.G. Mendiratta
Gen. Elec. R&D Center	AF	Ni_3Al+B	S.C. Huang
Pratt and Whitney			
E. Hartford	–	Ni_3Al	D. Duhl
W. Palm Beach	AF	$Fe_3Al+B, TiAl$	E. Slaughter
E. Hartford	AF	TiAl	M. Blackburn
Oak Ridge National Lab	DOE	$(FeNi)_3V,$ Ni_3Al+B	C.T. Liu
	ONR	Fe_3Al	C.T. Liu
Olin Corp.	Internal	Fe_3Al	--
Marko Materials	DARPA/AMMRC	FeAl+B	R.V. Ray
Univ. of Pennsylvania	NSF	Ni_3Al	D.P. Pope
	DOE-ORNL	$(FeNi)_3V$	D.P. Pope
Dartmouth Univ.	DOE-ORNL	Ni_3Al, Fe_3Al	E. Schulson
	NASA	NiAl	E. Schulson
Vanderbilt Univ.	DOE-ORNL	$(FeNi)_3V,$ Ni_3Al	J.J. Wert
Case Western Univ.	AF	Fe_3Al+B	K. Vedula
	NASA	FeAl, NiAl	K. Vedula
Stanford Univ.	NASA	CoAl, NiAl	W. Nix
Texas A&M Univ.	NASA	NiAl, CoAl, FeAl	A. Wolfenden
Rensselaer Polytech. Inst.	DOE-ORNL	$(FeNi)_3V,$ Ni_3Al+B	N.S. Stoloff
	ONR	Fe_3Al, Ni_3Al	N.S. Stoloff
Case Western Univ.	NSF	NiAl	R. Gibala
Northwestern Univ.	NSF	Au-Ni	J. B. Cohen

JAPANESE EFFORTS

Research on ordered alloys continues at a fast pace in Japan. The report of
a Japanese committee currently assessing the future of ordered alloy
research is to be completed soon; however, it is likely that the report will
have restricted distribution.

Names associated with Japanese research in the field over the past
several decades include S. Ogawa, D. Watanabe, M. Hirabayashi, S. Yamaguchi,
and H. Iwasaki. An early review of order-disorder behavior was authored by
Muto and Takagi (1955). Recent Japanese work on ordered alloys covers much
of the field. Some examples of the nature of this work will be cited here
and other specific references will be made throughout this report.

An active area of research has been concerned with the so-called anomalous temperature dependence of the flow stress of $L1_2$ superlattice structures. Wee and co-workers (Wee and Suzuki 1979, Wee et al. 1980) have interpreted their results for a variety of materials in terms of the stability of the $L1_2$ structure relative to the closely related DO_{22} and DO_{19} structures. In related work, Takeuchi and Kuramoto (1973) have developed a cross slip theory to explain the temperature dependence. The effect of stoichiometry on the flow stress of Ni_3Al and Ni_3Ga at 77°K and room temperature has been studied by Noguchi and co-workers (1981). The flow stress increases with changes in composition on both sides of stoichiometry, but the increase is greater on the excess aluminum or gallium side. Whether this effect is caused by changes in dislocation behavior and/or the development of defect solid solutions is not clear. Hanada and co-workers (1981) have related the high-temperature deformation behavior of Fe_3Al in both the B2 and DO_3 forms to composition, degree of order, and ease of cross slip. The degree of order and cross slip are thought to explain the peak in strength below T_c; above T_c the cross slip of B2 superlattice dislocations is thought to be controlling, with the differences in various peak temperatures cited in the literature caused by slight variations in compositions. The pioneering work by Aoki and Izumi (1979), which laid the foundation for the extensive work at Oak Ridge has established that normally brittle polycrystalline Ni_3Al can be ductilized by boron additions. Finally, creep in AgMg has been studied recently by Murakami and co-workers (1978) and Yamaguchi and Umakoshi (1979).

In the area of structural work, the order-disorder transformation and the ordering kinetics in Fe-Al alloys have been studied with x-ray diffraction (XRD) by Oki and co-workers (1973 and 1974), with transmission electron microscopy (TEM) by Sagane and co-workers (1977), and with Mossbauer techniques by Oki and co-workers (1979). The equilibrium phase diagram for the Fe-Al system has been approximated recently by Hasaka (1980) using calculations based on a pair-wise interaction model using interactions out to third neighbors.

In summary, ordered alloys are being very actively researched in Japan. High-quality structural and chemical characterization is an important strength of the Japanese research. It appears that the goal is to develop additional useful alloys in the near future and that a coordinated program is evolving to accomplish that goal.

SOVIET EFFORTS

Soviet research on ordered alloys began with the early work of Kurnakov and co-workers (1916). Extensive research since that time has involved such well-published researchers as W. Gorsky, A. Smirnov, M. Krivoglaz, N. Golosov, I. Seliisky, Y. Lifshits, L. Landau, A. Khachaturyan, L. Popov, V. Danilenko, E. Nesterenko, I. Kornilov, and V. Heychenko. The recent Soviet research is broad in scope and only some representative recent works will be cited here to give indications of current emphases.

There has been a continuing effort to calculate phase equilibria for various ordering systems, usually on the basis of a pair-wise interaction energy. For example, Danilenko and Nesterenko (1980) have calculated the ordering for an AC-BC quasi-binary for ternary alloys with the B2 structure. The results were compared to experiment for NiAl-FeAl. The energies of mixing for Fe-Ni-Al alloys have been calculated on the basis of sublattice occupancies (Zalutsky and Nesterenko 1979). The calculated ordering energies for atoms in the first- and second-neighbor positions increased with silicon content for alloys along $Fe_3Al - Fe_3Si$ (Katsnelson and Polishchuk 1974). A calculation of the Fe-Al equilibrium diagram based on a model with tetrahedral clusters has given qualitative agreement with experimental results in the literature (Golosov et al. 1976). In related work, the Ni-Al diagram has been calculated using a pseudopotential method (Portnoy et al. 1979) as has the ordering behavior of interstitial phases based on an hcp structure (Dmitriev et al. 1980). The electronic structures of alloys with LRO and SRO (Yegorushkin and Kulmentyev 1979) and partial order (Alyshev et al. 1981) also have been calculated.

A study of the kinetics of ordering in FeAl has shown that the rate decreases as the composition is changed from stoichiometric and that addition of silicon, copper, and chromium decreases the effect (Kucherenko and Troshkina 1980). Germanium has been found to increase the range over which Fe_3Al exists (Elyutin and Khachaturyan 1972). In the Fe-Al-Si system, the occurrence of multiple phases of $Fe_3(Al,Si)$, $Fe(Al,Si)$, and solid solution caused broadening of high-angle diffraction lines (Glezer et al. 1972). Calorimetry and magnetic susceptibility have been used to study atomic and magnetic disordering in Fe_3Al (Kravtsova et al. 1980 and 1982). Work also has been done on the Heusler type alloy Fe_2MnAl (Zalutsky et al. 1976). Phase diagram sections for additions of zirconium, tungsten, and molybdenum to Ti-alloys have been examined (Nartova et al. 1982). The general approach to studying phase equilibria based on TiAl and Ti_3Al has been discussed (Glazunov 1981). Mossbauer spectroscopy has been used to relate the strength of Ni-Al alloys to structure (Dorofeyev et al. 1979) and positron annihilation was used to study vacancies in off-stoichiometric CoAl and FeAl (Dekhtyar et al. 1979). Several studies have examined SRO in Fe-Al alloys (Dorofeyev and Litvinov 1978, Iveronova et al. 1973).

The temperature dependence of yield stress of Fe-Si and Fe-Al alloys has been related to the superlattice dislocation type, with this type thought to be dependent on the alloy composition (Glezer and Molotilov 1979). Popov and co-workers (1979) have examined the flow stress of Ni_3Fe as a function of temperature. The relation of various superlattice dislocation configurations to plastic behavior has been considered (Grinberg 1978, Kgornostyrev et al. 1981, Nosova 1981). Related to these deformation studies have been attempts to calculate diffraction contrast for TEM imaging of various APB configurations (Pikus and Glezer 1978). There have also been TEM studies of APB and dislocation mobility (Kozlov and Koneva 1978) and the causes of preferred orientation of APBs (Pushkareva et al. 1979). The formation of precipitates by heterogeneous nucleation on periodic APB in modified Cu_3Au has been studied by Sukhanov and co-workers (1980). The modification of Ni_3Al by alloying for structural use at high temperature (above 1100°C) has been reported by Portnoy and co-workers (1980 and 1981).

Other recent published works describe the effect of silicon on diffusion in Ni-Al alloys, where the interdiffusion coefficient increases toward pure nickel and with addition of 6 at% Si (Kositsyn et al. 1980), and the effect of titanium, hafnium, tantalum, niobium, and molybdenum on the sublimation of and diffusion in Ni_3Al (Bronfin and Drugova 1978). All elements decreased both the rate of evaporation and the diffusivity. Neutron irradiation of Fe_3Al has been studied by Ibragimov and co-workers (1982), and the optical properties of ordered and disordered Fe-45Al have been investigated by Kudryavtsev and Lezhnenko (1977). Finally, work on the synthesis of six different aluminides by high-temperature chemical reaction has been reported by Podergin and co-workers (1975).

There is considerable research activity on ordered alloys in the Soviet Union. Calculational approaches appear to be popular and some of this type of work appears good.

EUROPEAN RESEARCH ON ORDERED ALLOYS

The current research effort in Europe is now quite small. The main programs are at the University of Poitiers, France, under Rabier, at the University of Science and Technology in Lille, France, under Escaig, and at the University of Groningen, Holland, under DeHosson. In all three programs, the emphasis is on obtaining a scientific understanding of the deformation properties of complicated ordered alloys. None of these investigators has, to our knowledge, published work on the development of ductile polycrystalline ordered alloys. In addition, there is a program on titanium aluminides being carried out at the National Gas Turbine Establishment at Farnborough in the United Kingdom.

CONCLUDING REMARKS

Based on the information available in the open literature, the committee has concluded that coordinated efforts aimed at the development of new ordered alloys for structural applications are under way only in the United States and Japan. The two major efforts in the United States, at Wright-Patterson Air Force Base and at Oak Ridge National Laboratory, are, at present, the most productive and most highly successful. However, based on the quantity and quality of the publications from Japan, it is clear that substantial results also will soon come out of Japanese efforts.

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4

POTENTIAL DEPARTMENT OF DEFENSE APPLICATIONS

Inasmuch as current development programs are concentrating on alloys of nickel, titanium, or iron with aluminum, applications for these types of materials will be emphasized. The potential advantages of such alloys are their relatively low density coupled with good stiffness, strength, and oxidation characteristics, and uses that exploit such features must be sought. Components in powerplants and in certain airplanes are obvious candidates, especially for parts required to operate at high temperatures. It is recognized that additional projects are seeking to identify alloys with other attributes (e.g., wear resistance, magnetic properties, radiation resistance). Although space constraints prevent detailed consideration, much of the following discussion should apply equally well to these alloys.

To date, no ordered alloy has reached the stage of development at which sufficient manufacturing and design data have been generated to permit incorporation in defense systems. Consequently, it is not possible to attempt a correlation between specific alloys and specific applications. Many factors, however, influence such alloy selections, and identification of these factors will be useful not only in seeking applications but also in orienting development efforts to address such factors.

Even when engineering data are at hand, there is a series of contractual and administrative considerations that may impede the timely introduction of a new material into production. These include specifications from which approval for deviation would be required, sole source conditions to which many contractors might justifiably object, production schedules so tight that time for usage validation is not available before final commitment to full scale production is required, and poor part performance, which encourages conservatism on the contractors part. Component selection for early ductile ordered alloy application should attempt to minimize these factors.

APPLICATIONS OF NEW ALLOYS

It is sometimes assumed that the existence of a new alloy that exhibits
properties better than those currently available will be sufficient to
justify its application since it will improve system performance. However,
the factors that must be considered are many and complex, and include
performance specifications and various elements of cost. The following
paragraphs deal with some of these considerations.

Performance and Cost Specifications

Most vehicles or equipment that could utilize ordered alloys will be
designed to meet a specific set of comprehensive requirements (e.g., weight,
thrust, speed). With these specifications established, the designer must
not only meet these requirements but also strive to ensure that the system
can be built on schedule and within cost. Thus, improved performance over
and above the goal is not necessarily an advantage even in military aircraft
where performance is so important. There is no incentive to exceed the
requirements unless it can be done with no increase in cost and no
compromise in reliability. To an extent, materials of construction are set
by the specification; given a choice, a designer will select a proven cheap
alloy. However, cost-weight trade-offs will have to be made for each system
so a new material can buy its way in, assuming the risk factors are deemed
acceptable. Risk is made up of several considerations ranging from fear of
the unknown to the fact that only a limited amount of characterization has
been performed and only a small amount of mechanical property data may be
available. This last point can serve to introduce another important
factor: In the development of new alloy systems, tensile strength is often
the only property determined. Increases in strength may be useful but it
represents only one potential limiting characteristic.

Limit Conditions or Failure Modes

Estimates of the structural advantage of a new material are frequently made
by relating specific strength (strength:density) to component size. Using
such a method, an alloy that is twice as strong will result in a part half
as thick or an alloy half as dense will cut the weight in half. This will
be true only if all the key properties of the alloy do not result in a
change in failure mode. In typical aircraft structures, a variety of limit
conditions may be encountered (e.g., overload, buckling, fatigue). Each can
serve to size the part. It is clear, therefore, that weight reduction made
possible by an improvement in one property can be restricted to a point
where another failure mode becomes critical. This is illustrated in
Figure 12 (Ekvall et al. 1982) which shows the required structural
thicknesses to sustain the various failure limits in an aircraft structure
built of two competitive materials. The original alloy (shown on the left),
limited by strength, is compared with a new alloy (shown on the right) for
which the limit is set by damage tolerance. In the development of ordered
alloys it will be important to consider the balance of properties that can
be achieved. Improvement in one property may not yield a commensurate
component benefit should other properties change. Evaluation of the
resistance of new alloys to a spectrum of test conditions will be required
to permit the determination of application potential. This type of
evaluation unfortunately should not be relegated to the later stages of a
development program.
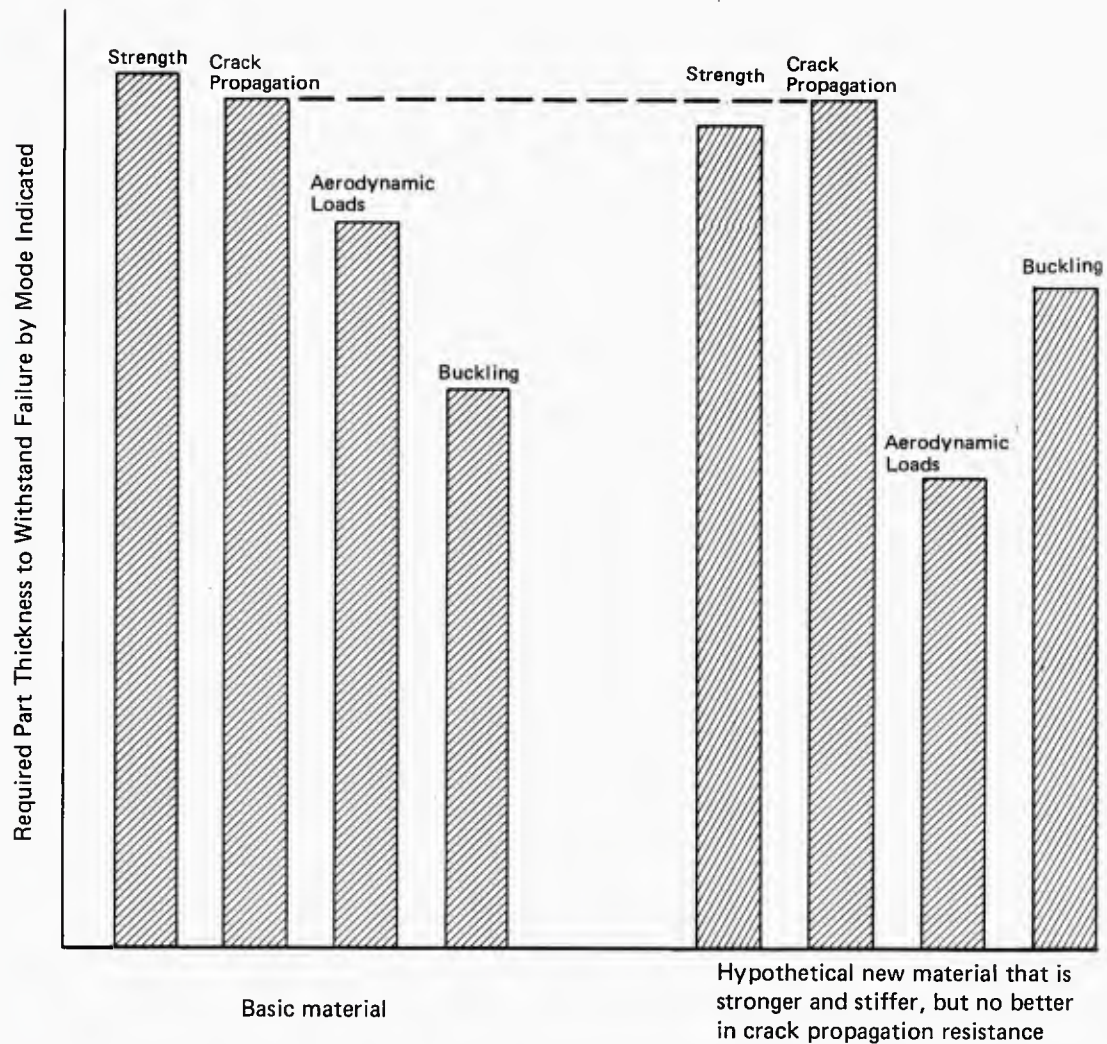
FIGURE 12 Potential weight savings considering additional failure modes (based on Ekvall 1982).

Timing Constraints and Application Windows

A review of the Department of Defense planning documents about two years ago
yielded a list of projected major new systems scheduled for production
between 1983 and 2000 (Kearns 1982). Details are given in Table 7; the
numbers although subject to change are of the right order of magnitude and
would seem to offer many opportunities for new materials. However, timing
constraints alter this assessment because of the qualification requirements,
and these constraints vary widely depending on whether the material is to be
included: in the original design, during the design phase, to correct a
test deficiency, or to alleviate a service problem.

The original concept of high-performance systems usually precedes first
production by at least 10 years. Many of those listed in Table 7 have
already passed this conceptual stage and, therefore, application windows
have apparently been closed. However, high-performance vehicles often
experience unacceptable weight increases during prototype development, and
component failures also are not uncommon at this stage. Such occurrences
offer additional opportunities for the application of new materials.
Problems in service due to unanticipated operational conditions often arise
and these, depending on the magnitude of the problem, could result in
materials substitutions. In Figure 13, the potential application
opportunities in airframes and engines are indicated by arrows at the
appropriate times.

TABLE 7   New Systems in the Department of Defense Plans

Year	A/C[a]	M[b]	LV[c]	S[d]	Other[e]
1983	2	1	–	–	–
1984	1	1	–	–	–
1986	–	2	–	–	–
1987	2	1	6	4	1
1988	3	3	1	1	–
1989	4	2	1	3	–
1990	2	1	–	1	1
1991	1	2	–	5	–
1992	1	3	–	–	–
1993	1	2	2	1	–
1994	2	–	3	–	1
1996	1	–	–	–	–
2000	2	–	–	–	–

[a]Fixed-wing aircraft and helicopter.
[b]Missiles.
[c]Land vehicles.
[d]Ships and other seaborn vehicles.
[e]Guns, etc.
SOURCE: Kearns (1982).

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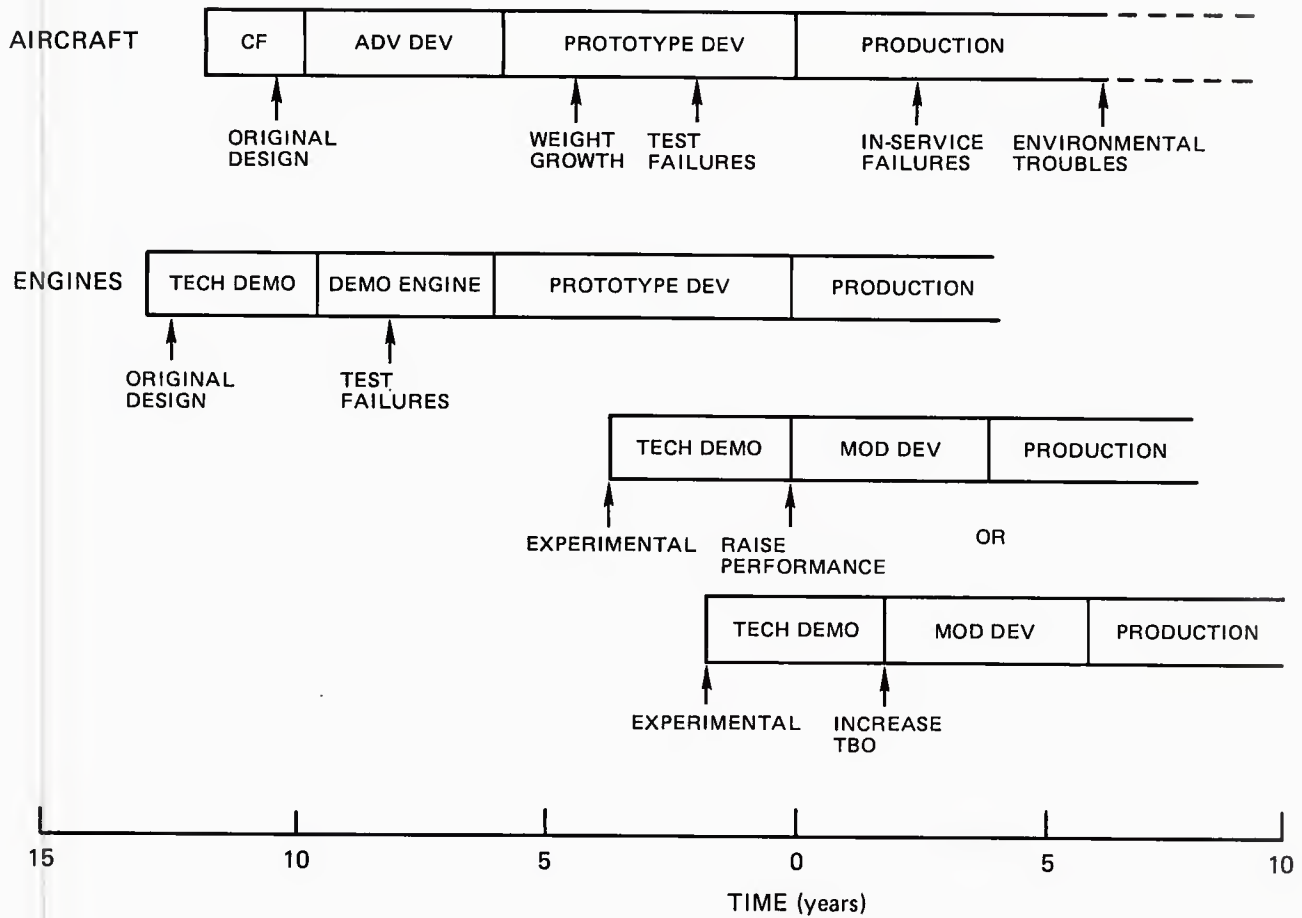
FIGURE 13 New material application windows (Ekvall et al. 1982).

QUALIFICATION AND INCORPORATION PLANNING FOR NEW MATERIALS

Having indicated some of the problems that will be encountered in gaining acceptance of a new material and getting it incorporated into systems, it may be informative to examine how this has occurred in practice. If the materials used in the various systems and equipment operated by the armed forces are surveyed, it becomes clear that new and upgraded materials are incorporated on a regular basis. Some of the changes are obviously evolutionary, but it is the more revolutionary changes that are of interest here. There are a series of steps through which a (successful) new material must pass on the way to qualification. These are represented in Figure 14, which shows not only the timing of these stages but also the approximate cost. Based on the first inception of a new idea, a series of laboratory tests usually is performed to confirm the promise of the system and define basic capabilities; this is a relatively inexpensive stage. The development stage is much more costly and involves processing studies (e.g., large-scale melting, conversion to mill products), development of preliminary design property data, fabrication trials, etc. Assuming success at this stage, prototype hardware would next be produced and subjected to rig, engine, and, in some cases, service tests. In parallel, qualification of alternate production sources would occur and for incorporation approval would be sought from the various control agencies. Finally, after 10 or more years and the expenditure of about $15 million, components made from the new material would be incorporated into production hardware.

It is obvious that such a complex development sequence involves many participants--the customer, the manufacturer, vendors, technical laboratories, etc. Even these descriptive titles are in some ways misleading in that parties are concerned with many aspects of the activities. For example, government agencies often fund much of the initial screening program through to manufacturing technology demonstrations before the material is incorporated into a product acquired by DOD. In many cases close coordination of all stages aids greatly in providing periodic feedback and program continuity. The other important, and often less tangible, factor that is created by such a team is an advocate (or advocates) of the technology in the key manufacturer and customer areas. Without such advocates, a technology can wither away and die in the current competitive atmosphere.

Another key element for any major thrust is frequent reviews of the payoff for the technology. If this is high, it obviously will serve to maintain momentum especially in times of technical tribulation. Such cost-benefit studies need to be repeated at regular intervals, especially in the time period between the euphoria of laboratory demonstration and the bleak realism of the development program, because the baseline assumptions often are modified as new information becomes available. It is well to remember that the first thing you ever hear about a new material is the best.

The situation can be summarized, in relation to the above scenario, for the new alloys that have been covered in presentations to the committee:

1. Titanium aluminides--Development path is well under way. If basic engineering concerns can be overcome, limited engine utilization could occur as early as 1987.
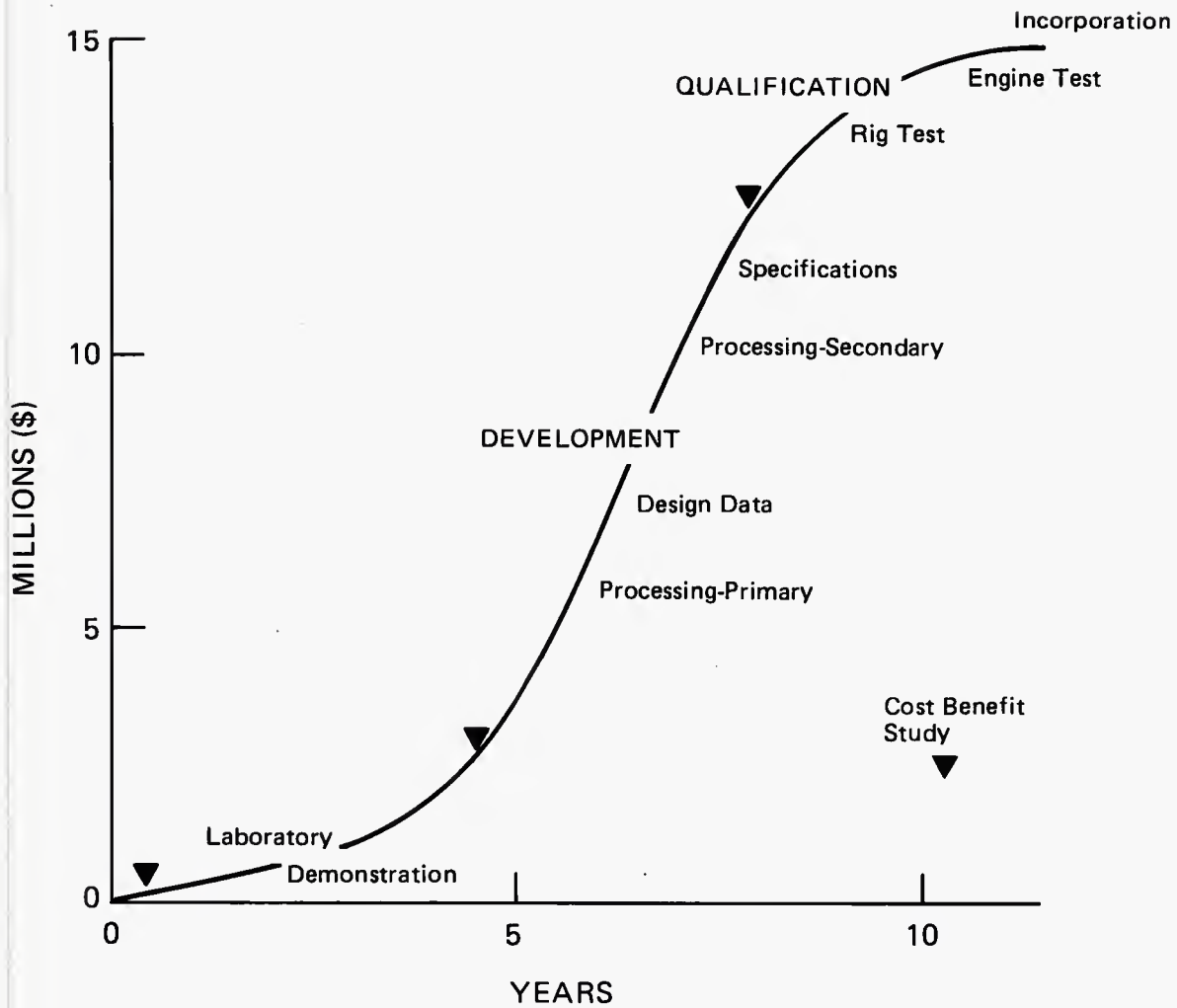
FIGURE 14 Typical development sequence for a new material being incorporated into a defense system (courtesy of United Technologies, Inc., Pratt and Whitney Aircraft).

2. Iron aluminides--Preliminary laboratory demonstration is nearing completion. If systems pass cost-benefit tests, they should proceed to development stage within three years with qualification possible by 1990.

3. Nickel aluminides--Laboratory demonstration has been initiated and results have been promising. Some preliminary component identification has been performed, but more is needed. Clearer picture of payoffs will be required in the future.

4. Iron-base ordered alloys--Laboratory demonstrations have shown some attractive properties. Lack of potential user interest and specific payoffs seem to be major drawbacks at present.

SOME POTENTIAL APPLICATIONS

Based on the known characteristics of the alloys that have been covered in this review, the most obvious applications are in gas turbine engines. The intermediate- and high-temperature strength characteristics, low density, etc., all point to such applications. Material temperatures encountered in propulsion systems of this type are characteristically high. Alloys with good high-temperature strength and oxidation resistance and low density would seem especially advantageous in rotating parts in which centrifugal loads may account for about 75 percent of the total loading. Figure 15 illustrates a typical large transport aircraft turbofan engine and Table 8 lists property requirements and failure modes possible for the various components.

Potential applications for the various classes of ordered alloys, especially the aluminide systems, are covered in more detail below with emphasis on rotating components. The illustrations chosen also include brief descriptions of the extremes in operating conditions together with the materials and processes used to make the components.

Requirements for fan and low pressure compressor parts, shown in Figure 16, are low density but high stiffness and strength. These characteristics seem best fitted by the titanium aluminides. The front end of an engine operates at low temperatures and is subject to the ingestion of foreign objects. Thus the basic damage tolerance of any aluminide system would have to be shown to be adequate. Temperatures rise rapidly as one proceeds through the high pressure compressor, shown in Figure 17, and several of the ordered alloy systems could be considered for these components. Weight, durability, and the fire danger will dictate the specific alloy selected. It is probable that a combination of systems would be the best compromise. It should be noted that the drum rotor design requires good welding and repair characteristics.

The burner, Figure 18, and high pressure turbine, Figure 19, of gas turbine engines represent the most challenging environment for materials. Stresses and temperatures are high, but maximum values usually do not occur simultaneously, leading to complex durability (thermo-mechanical fatigue) requirements. Nickel aluminides are the only current candidates that have any prospect of meeting the mechanical and corrosion properties needed in
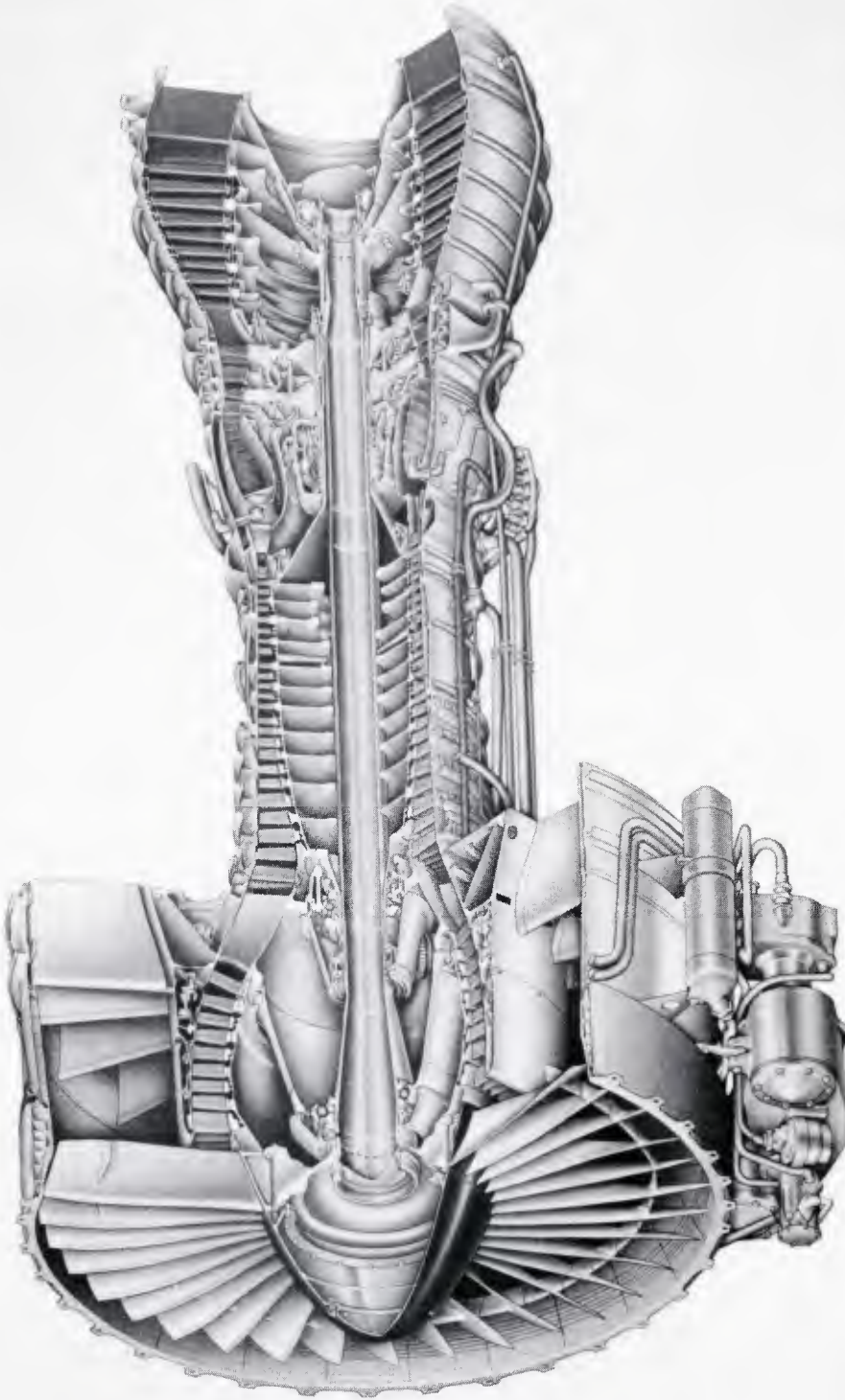
FIGURE 15 Aircraft turbofan engine (courtesy of United Technologies Corporation, Pratt and Whitney Aircraft).

TABLE 8 Gas Turbine Engine Metal Components — Material Property Requirements and Failure Modes

Component	Major Material Property Requirements	Typical Failure Modes
Compressor disks (incl. fan)	High specific strength; creep resistance; stiffness; fatigue (LCF/crack growth); oxidation/corrosion resistance; weldability	Low cycle fatigue
Compressor blades	Fatigue (LCF/HCF); stiffness; low density; erosion resistance	LCF and HCF; foreign object damage; fire/overheating
Cases (fan and compressor)	Strength; creep resistance; fatigue; dimensional stability; repairability	Low cycle fatigue; impact damage
Shafts	High specific strength; fatigue resistance; creep resistance	LCF; wear
Combustor liner	High burnout temperature; thermal fatigue strength; oxidation and hot-corrosion resistance; creep resistance; fabricability; repairability	Thermal fatigue; creep-buckling; burn-through; HCF
Turbine vane	High burnout temperature; fracture toughness; thermal fatigue strength; oxidation and hot-corrosion resistance; erosion resistance; low distortion; repairability	Thermal fatigue; oxidation; hot-corrosion; distortion (creep)
Turbine blade	High burnout temperature; tensile strength (yield and ultimate); stress-rupture life; creep resistance; oxidation and hot-corrosion resistance; fatigue strength (HCF and LCF); fracture toughness; erosion resistance; low thermal expansion; high thermal conductivity; low density; repairability	Stress-rupture; oxidation; hot-corrosion; thermal fatigue; HCF
Turbine disc	Rim: stress-rupture life; creep resistance; fatigue strength (LCF); oxidation and hot-corrosion resistance Hub: tensile strength (yield and ultimate); fatigue strength (LCF); low density for entire disc	Mechanical LCF; HCF
Cases (diffusion and turbine)	Tensile strength (yield and ultimate); stress-rupture life; creep resistance; fatigue strength (LCF); oxidation and hot-corrosion resistance; low distortion in blade region; fabricability; repairability	LCF (mostly mechanical) HCF
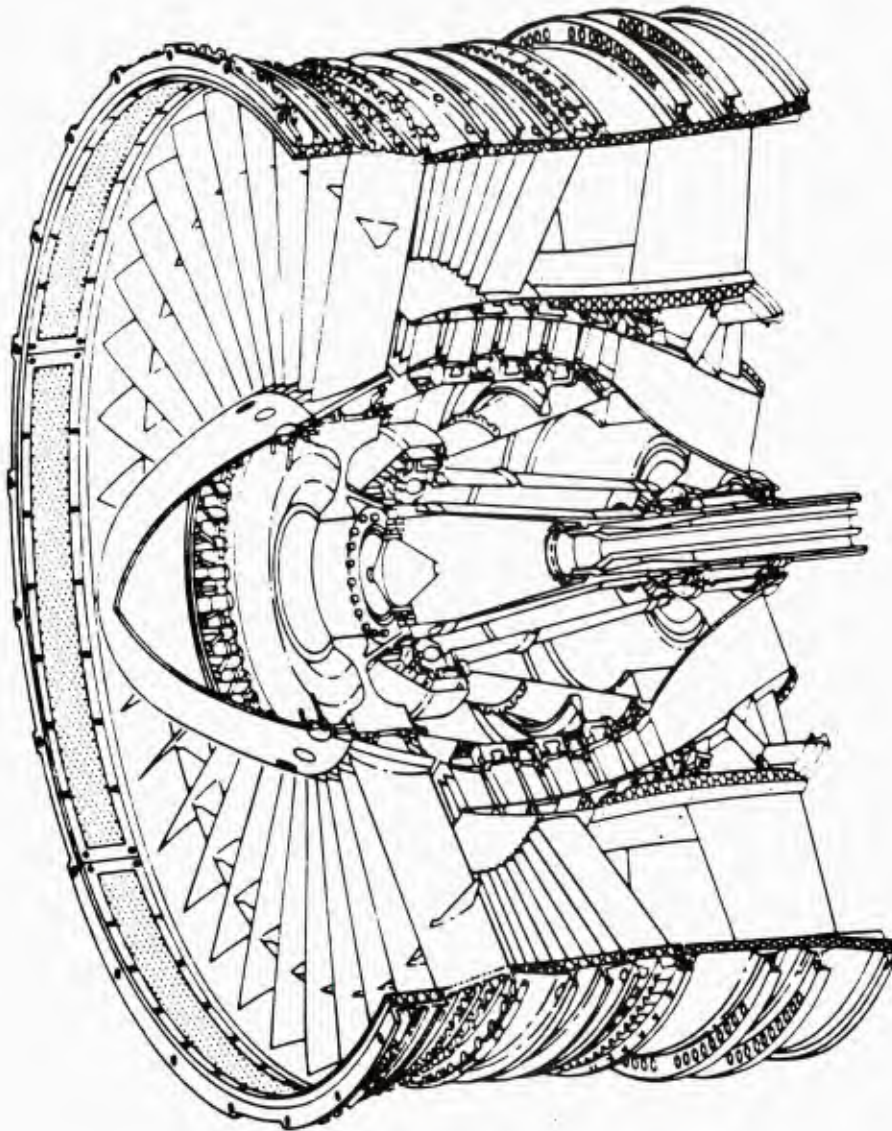
FIGURE 16 Fan assembly of a CF6-80 engine (courtesy of General Electric Company).
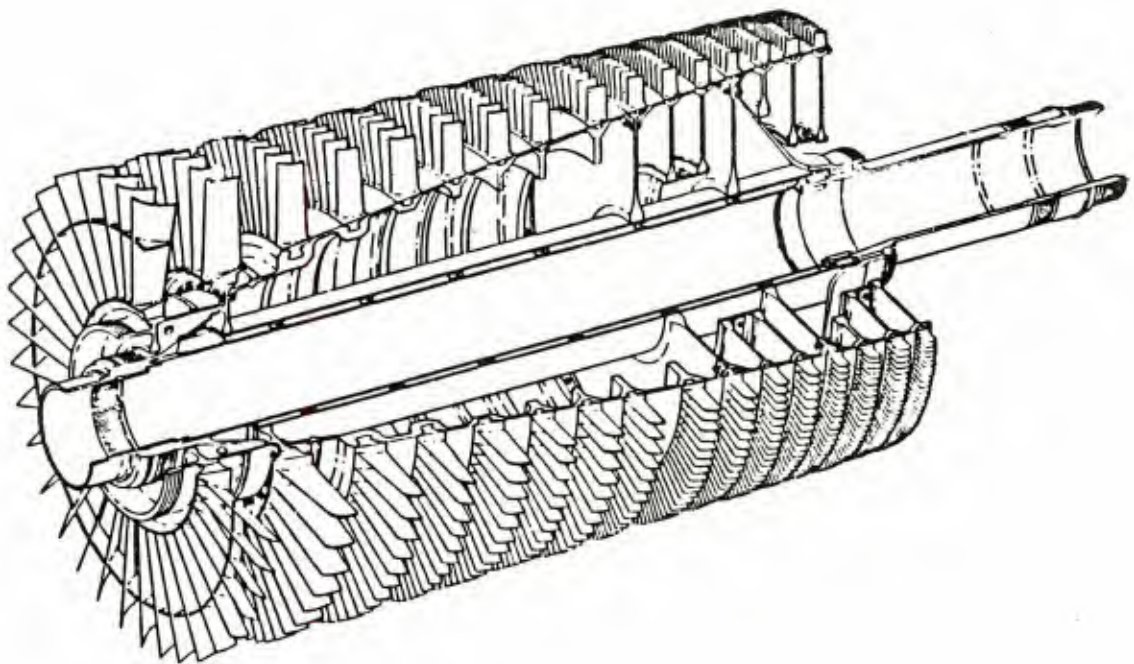
FIGURE 17   Compressor rotor of a CF6-6 engine (courtesy of General Electric Company).
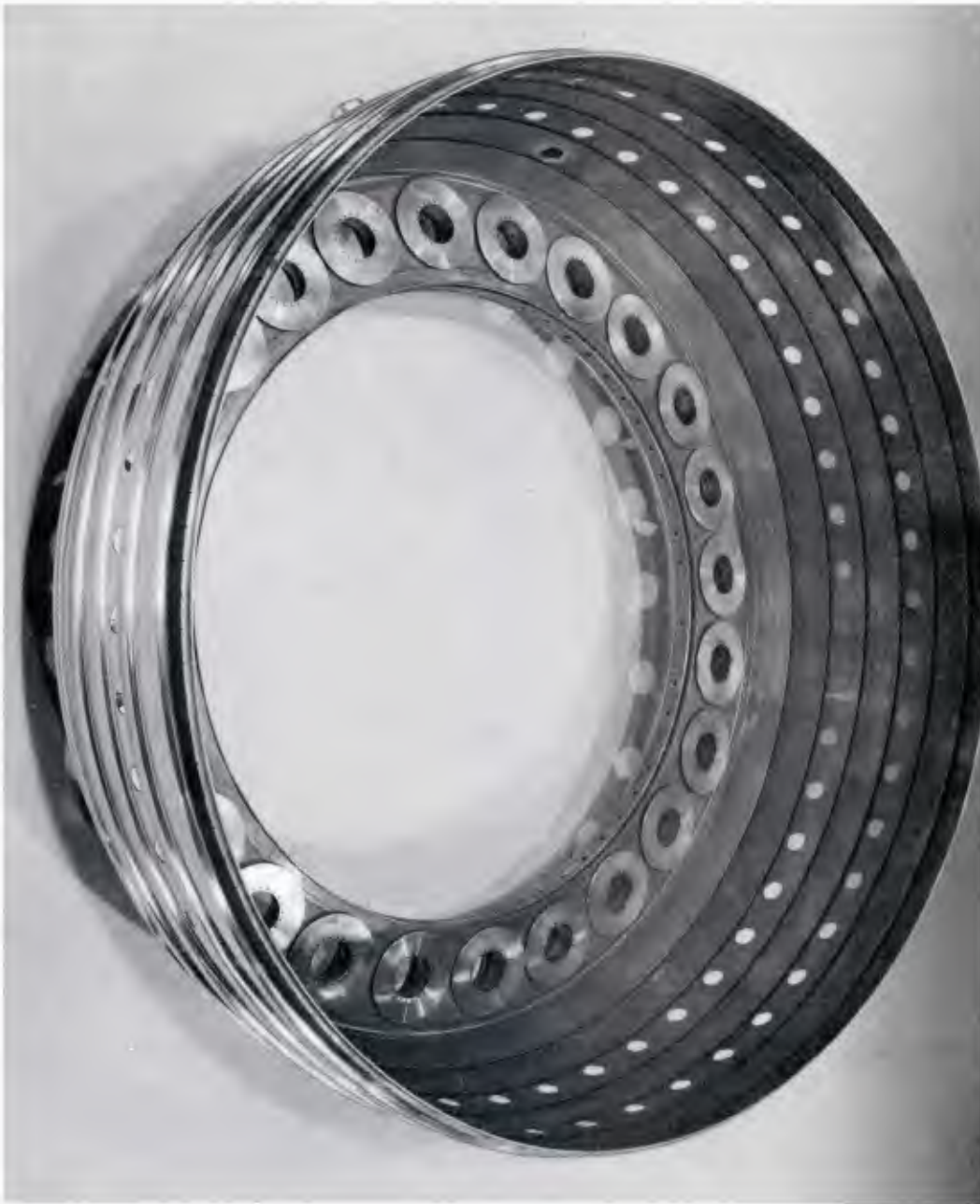
FIGURE 18   Combustion chamber of a JT9D engine (courtesy of United Technologies Corporation, Pratt and Whitney Aircraft).
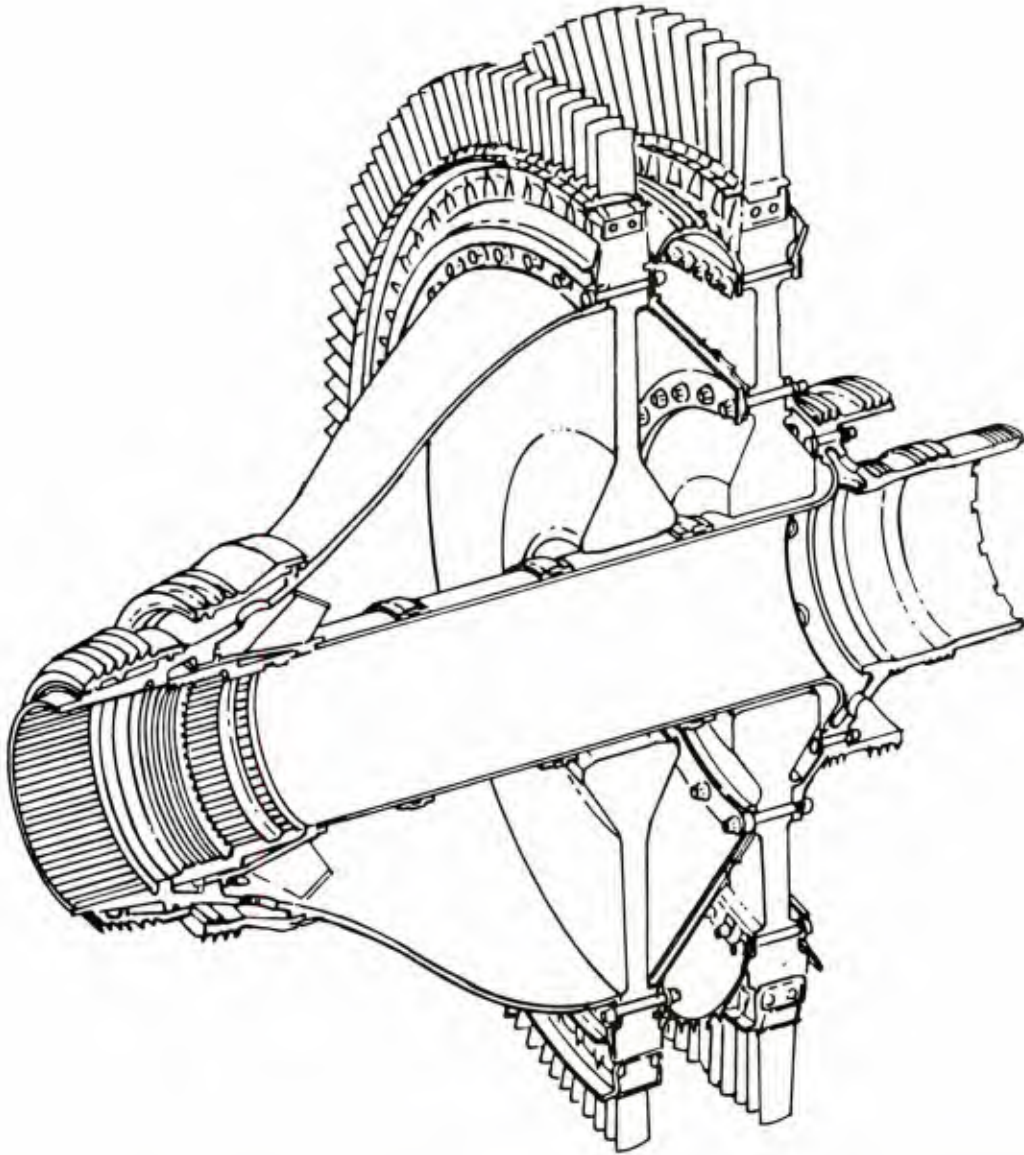
FIGURE 19 High pressure turbine assembly of a CF6-50 engine (courtesy of General Electric Corporation).

turbine disks, blades, and vanes. It is possible that the lower stresses that prevail in the burner could permit the exploitation of the excellent oxidation resistance of the iron aluminides. Components are presently made by a variety of methods and the ability to create these complex shapes from these new systems will also be a key factor. An example are the complex hollow blade and vane castings shown in Figure 20. The temperatures and, to a lesser extent, stresses are lower in the low pressure turbine (Figure 21), and the less demanding conditions open up several potential applications. Both the titanium and nickel aluminides appear candidates for disks and blades.

It is obvious from Figure 15 and the other illustrations that there are many other components in a turbine engine. The payoffs, compatibility with design needs, etc., would have to be assessed individually to define applicability. It is hoped that this rather brief treatment of some of the challenges for new material set by gas turbines will stimulate more in-depth studies.

A role for ordered alloys in rocket propulsion systems also can be foreseen if improvements over existing nickel-base superalloys are achieved. Of particular interest would be a thermal-fatigue and high-cycle-fatigue resistance superior to that of the MAR-M246 currently used for turbine blades on the Space Shuttle main engine, for example. Figures 22 and 23 show typical cross-sections of advanced rocket engine turbomachinery with potential applications being turbine blades, disks, and combustion chamber liners.

Other potential aerospace hardware applications for ordered alloys are in advanced metallic thermal protection systems and hot gas ducting for lift augmentation devices. In these last two cases, low density is of paramount importance, making the titanium aluminides of great interest.

Another possible application for advanced ductile ordered alloys is in nuclear space power systems. Several alternate system types are currently under study, and the maximum temperature to which structural materials will be exposed varies from one design to another. However, maximum temperatures would typically be in the range of 830 to 1230°C. Since these are flight systems, weight is an important parameter and materials that offer strength-to-weight advantages are attractive. The ductile ordered alloys currently being developed will not be adequate for use in the higher temperature systems being studied (i.e., maximum temperature of 1230°C); however, other alloy systems, such as the CoAl-base alloys, may be useful in the higher temperature ranges.

The space power systems based on the use of in-core thermionic conversion expose structural materials to lower maximum temperatures (i.e., 830°C). In these systems, the ductile aluminides, for example, could play a useful role in components such as the radiator, piping, pumps, manifolds, and nozzles.

To be applied in space power systems, materials must be compatible with the heat transfer fluids (typically molten metals such as lithium, sodium, or sodium/potassium). Limited experiments have shown good compatibility for

VANE
BLADE

FIGURE 20 Turbine blades and vanes of a PW2037 engine (courtesy of United Technologies Corporation, Pratt and Whitney Aircraft).
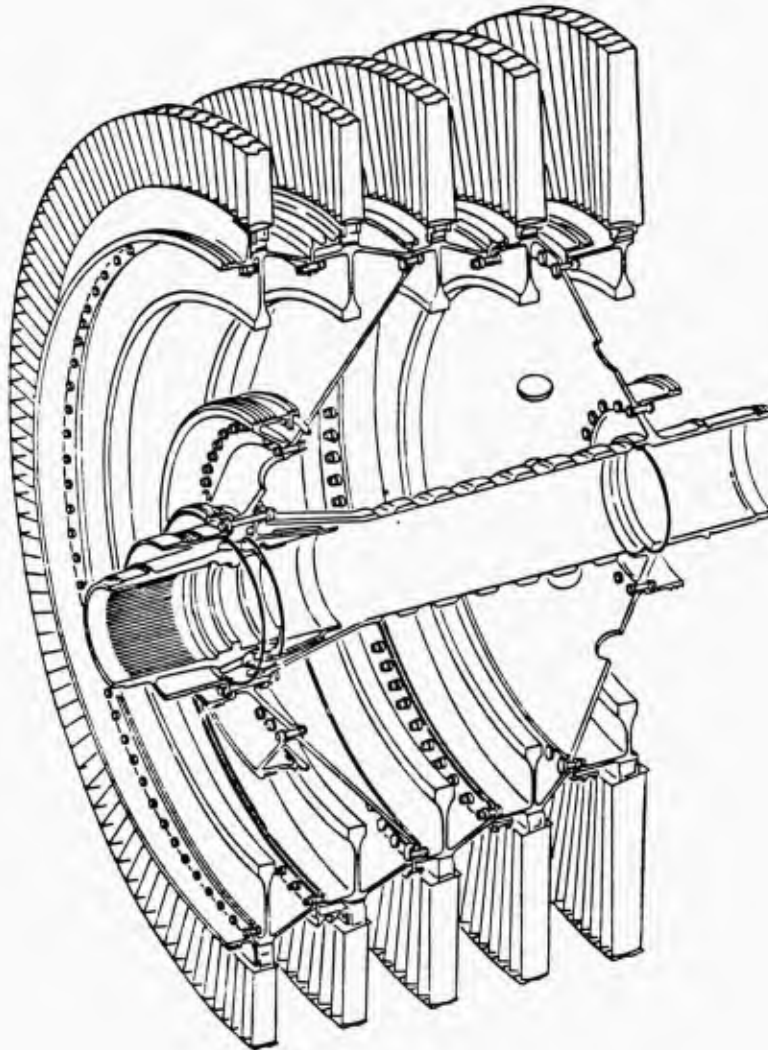
FIGURE 21 Low pressure turbine assembly of a CF6-6 engine (courtesy of General Electric Corporation).
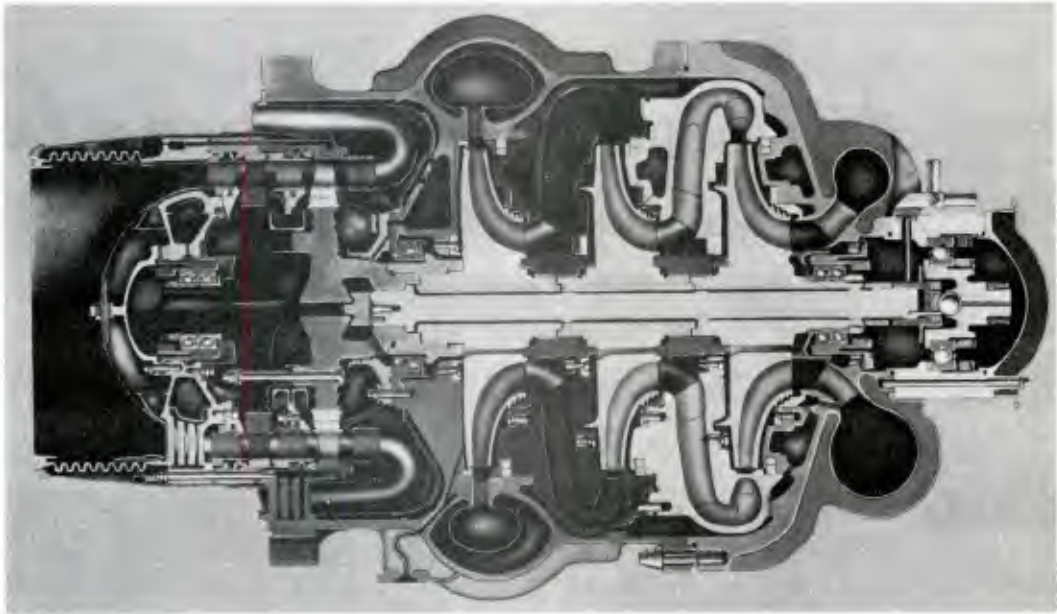
FIGURE 22   High pressure fuel turbopump (courtesy of Rockwell International, Rocketdyne Division).
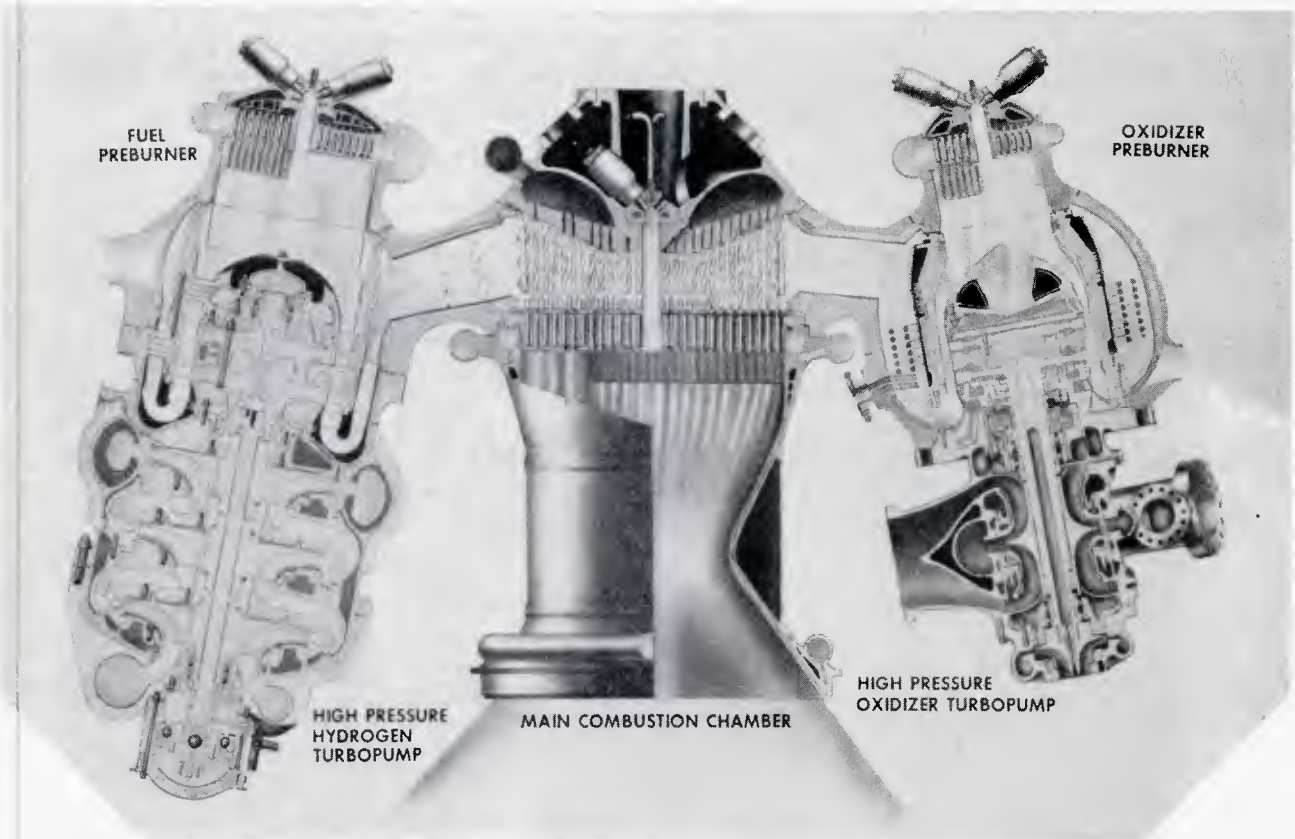
FIGURE 23 Space shuttle main engine powerhead component arrangement (courtesy of Rockwell International, Rocketdyne Division).

some ordered alloys with such molten alloys. The high nickel content of
some of the higher strength ductile ordered alloys may be a disadvantage in
this respect since many alloys with a high nickel content exhibit high
corrosion rates in liquid metals of the types indicated. Good resistance to
irradiation damage will be important for applications in shielded locations,
and the boron content of some of the high-strength ductile ordered alloys
may be a disadvantage in this regard. In addition, since space power
systems are typically fabricated from formed and joined sheet, pipe, etc.,
good fabricability and weldability will be required. Overall, however, the
weight saving potential of some of the ductile ordered alloys suggests that
they should be evaluated for space power.

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AVAILABLE DATA ON DUCTILE ORDERED ALLOYS

ENGINEERING DATA

Introduction

For materials to be useful in the high-reliability, precision-engineered structures typical of advanced defense technology systems, a very large body of pertinent engineering data must be available. Detailed specifications to ensure that procured materials exhibit acceptable degrees of reproducibility and predictability also must be available. The types of engineering property data that may be required include:

1. Physical Properties
    a. Modulus
    b. Thermal expansivity
    c. Thermal conductivity
    d. Density
    e. Specific heat
    f. Poisson's ratio

2. Time Independent Mechanical Properties
    a. Yield and tensile strength
    b. Tensile flow behavior
    c. Ductility
    d. Influence of multiaxial stressing
    e. Toughness

3. Time and Cycle Dependent Mechanical Properties
    a. Creep and rupture strength
    b. Creep-rupture ductility
    c. Low cycle fatigue strength (strain and load controlled)
    d. High-cycle fatigue strength (various R ratios)
    e. Creep-fatigue (thermomechanical fatigue)
    f. Effects of multiaxial stresses

    g. Slow crack growth due to fatigue, creep, creep fatigue, or static fatigue

    h. Effects of long-term thermal aging

    i. Size effect

4. Environmental Compatibility
   a. Oxidation
   b. Sulfidation behavior
   c. Stress corrosion cracking
   d. Evaporation rates in hard vacuum
   e. Susceptability to saline-bearing environment
   f. Erosion
   g. Corrosion by heat transfer fluids (liquid metals, water, steam, salts)
   h. Hydrogen embrittlement
   i. Tribology behavior at all operating temperatures
   j. Irradiation

5. Fabricability
   a. Ability to make required product forms
   b. Reproducible properties from production size lots for required forms
   c. Acceptable machinability
   d. Joinability (by welding, brazing, diffusion bonding)
   e. Acceptable formability
   f. Effects of form, forming, and joining on properties

    The relative importance of these properties change very substantially as a function of specific application. For example, in modest-temperature aerospace applications, density, modulus, tensile strength, and fatigue properties may be most important. In higher temperature applications, on the other hand, time- and cycle-dependent mechanical properties such as creep and rupture strength, creep-fatigue, and slow crack growth may be most important. Environmental compatibility requirements will vary greatly with application. In high-temperature jet engine applications, oxidation and sulfidation rates may be most important whereas in nuclear space power applications, liquid metal compatibility and evaporation rates in high vacuum may assume more significant roles. Clearly, for any of these applications, it is necessary for the materials to be available in the required shapes, and they must be joinable and machinable to the extent that this is a design requirement.

    In order to produce high-reliability designs it also is necessary to know the range of variability that can be expected in properties as a function of heat-to-heat variation, product form, etc. Typical requirements from MIL Handbook 5, in this respect, are shown in Table 9. For certain materials it also is necessary to assess properties as a function of directionality (anisotropy), which may vary considerably with product form.

    Overall, therefore, the qualification of an alloy for advanced defense system applications is a relatively expensive and time-consuming activity (see Figure 14) that is only undertaken when sufficient cost-benefit incentives exist.

TABLE 9 Typical MIL Handbook 5 Data Requirements

Feature	Required
Specification	Military, federal, or aerospace material specification
Room Temperature Values	Tensile, compression, shear and bearing tests on 10 lots from at least 2 production heats
Temperature Effects	Tensile, compression, shear and bearing tests on 5 lots from 2 heats at each temperature
Fatigue	No minimum data requirements
Creep and Rupture	At least 3 temperatures and 3 stresses covering 2 to 3 orders of magnitude on elapsed time for a minimum of 5 lots of material
Other	Effects of aging--properties of joints, physical properties, fracture toughness, stress corrosion

Available Data on Ductile Ordered Alloys

In the remainder of this section the discussion will be limited to the ductile ordered alloys recently developed at ORNL; specifically, most of the discussion will relate to the ductile Ni_3Al-based alloys. The currently available data on the engineering properties of ductile ordered alloys are extremely limited. In fact, most of the available information is for experimental lots of material and essentially no engineering type data exist. The data that are available, however, indicate that some of the ductile ordered alloys appear to possess properties that offer a considerable engineering advantage. The density-compensated yield strength and ultimate tensile strength of the ductilized Ni_3Al alloys, for example, increase with temperature and can achieve levels comparable to those of some of the highest strength alloys currently available (Figure 24 and 25) (Engineering Alloys Digest Inc. 1968; Menon and Reimann 1975; Conway and Stentz, 1980; and private communication with C. T. Liu, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983). Strengths of this order, coupled with fairly good ductilities, are encouraging.

The available data on creep and rupture behavior are very limited, but, again, encouraging. As indicated in Figure 26, the rupture strengths of the advanced LRO and aluminide alloys are well above those of many commercially available wrought alloys--and may approach the strength levels of some of the cast-nickel-base superalloys (Engineering Alloys Digest 1968; Menon and Reimann 1975; private communication with C. T. Liu, Oak Ridge National
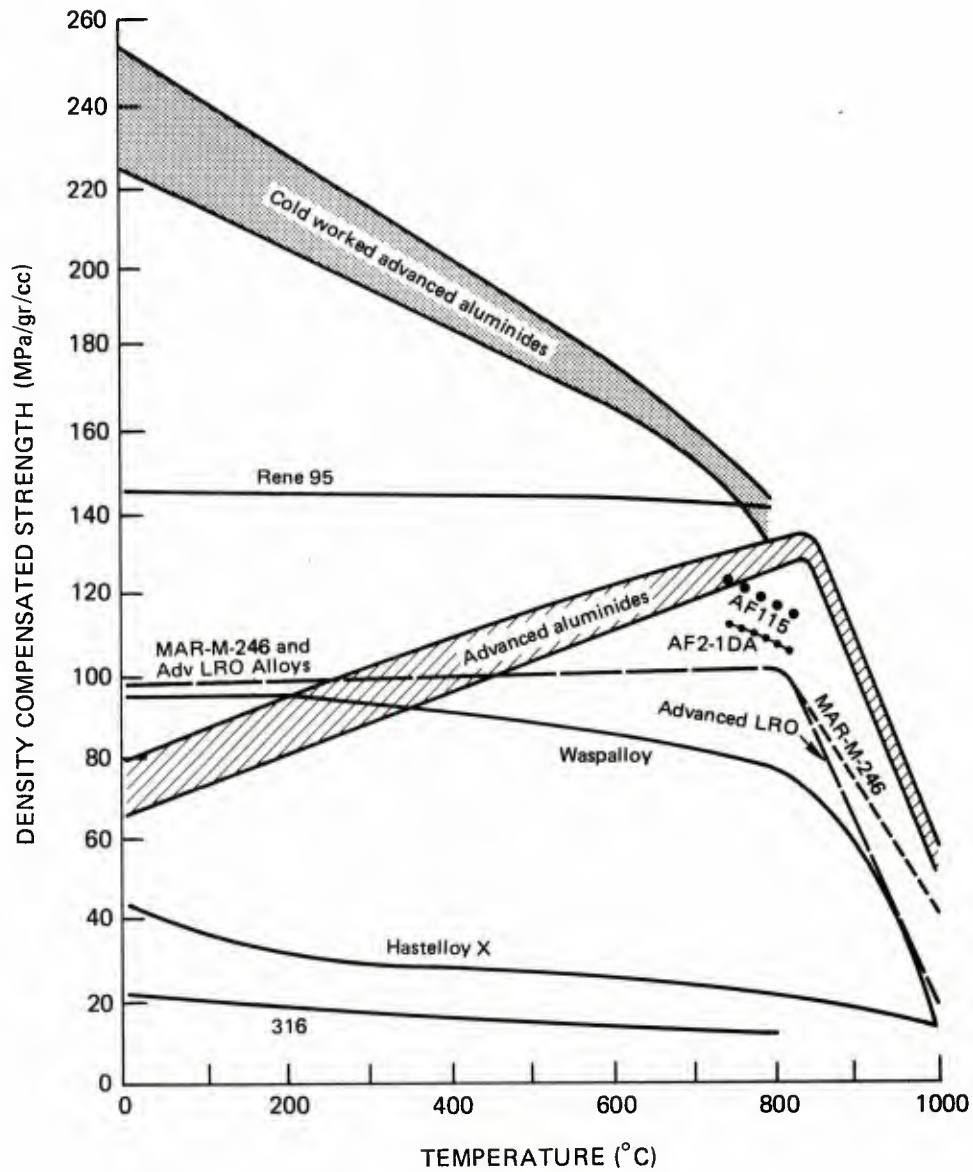
FIGURE 24 Comparison of the density-compensated yield strength of advanced LRO alloy and nickel aluminides with commercial structural alloys.
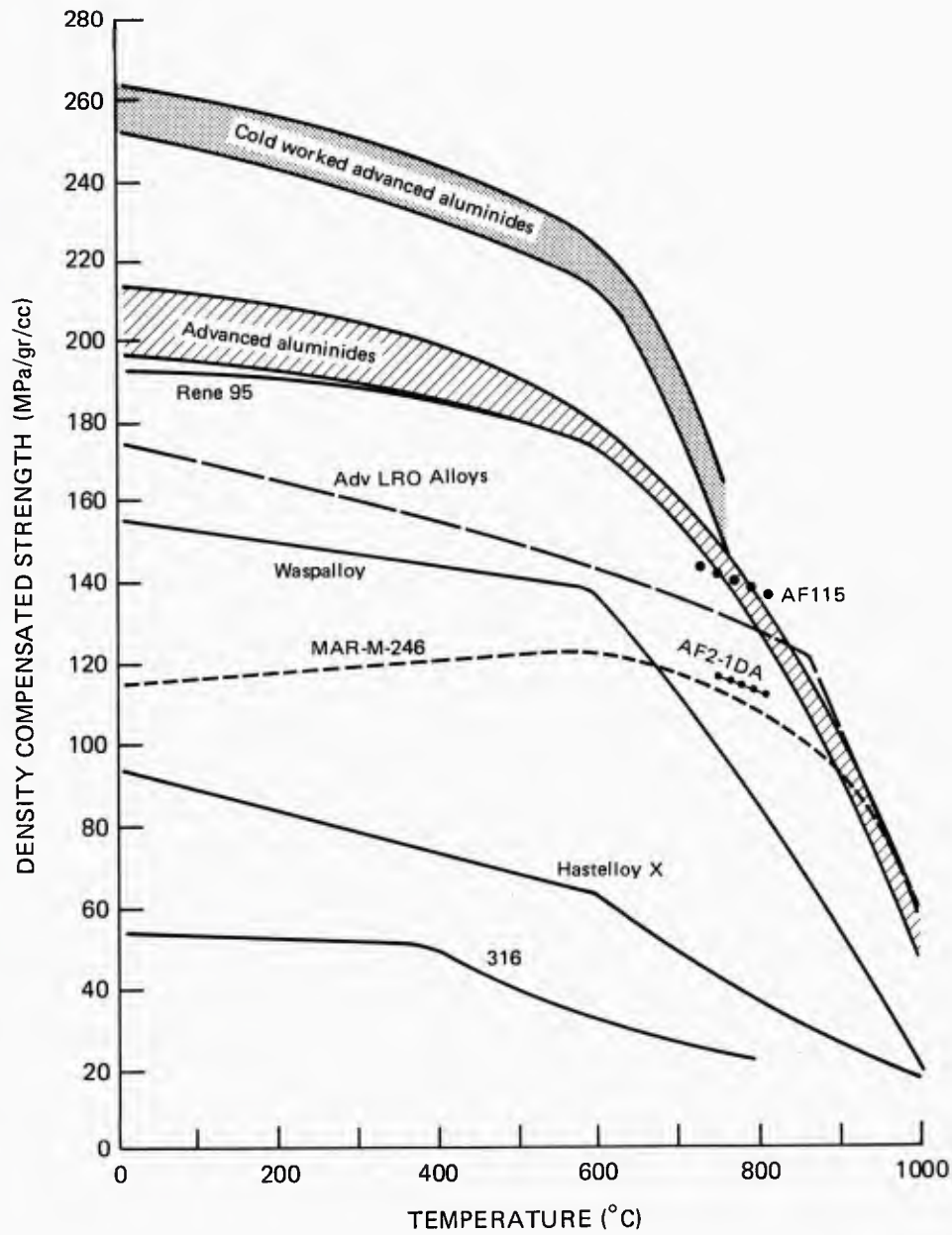
FIGURE 25 Comparison of the density-compensated ultimate tensile strength of advanced LRO alloys and advanced nickel aluminides with commercial structural alloys.
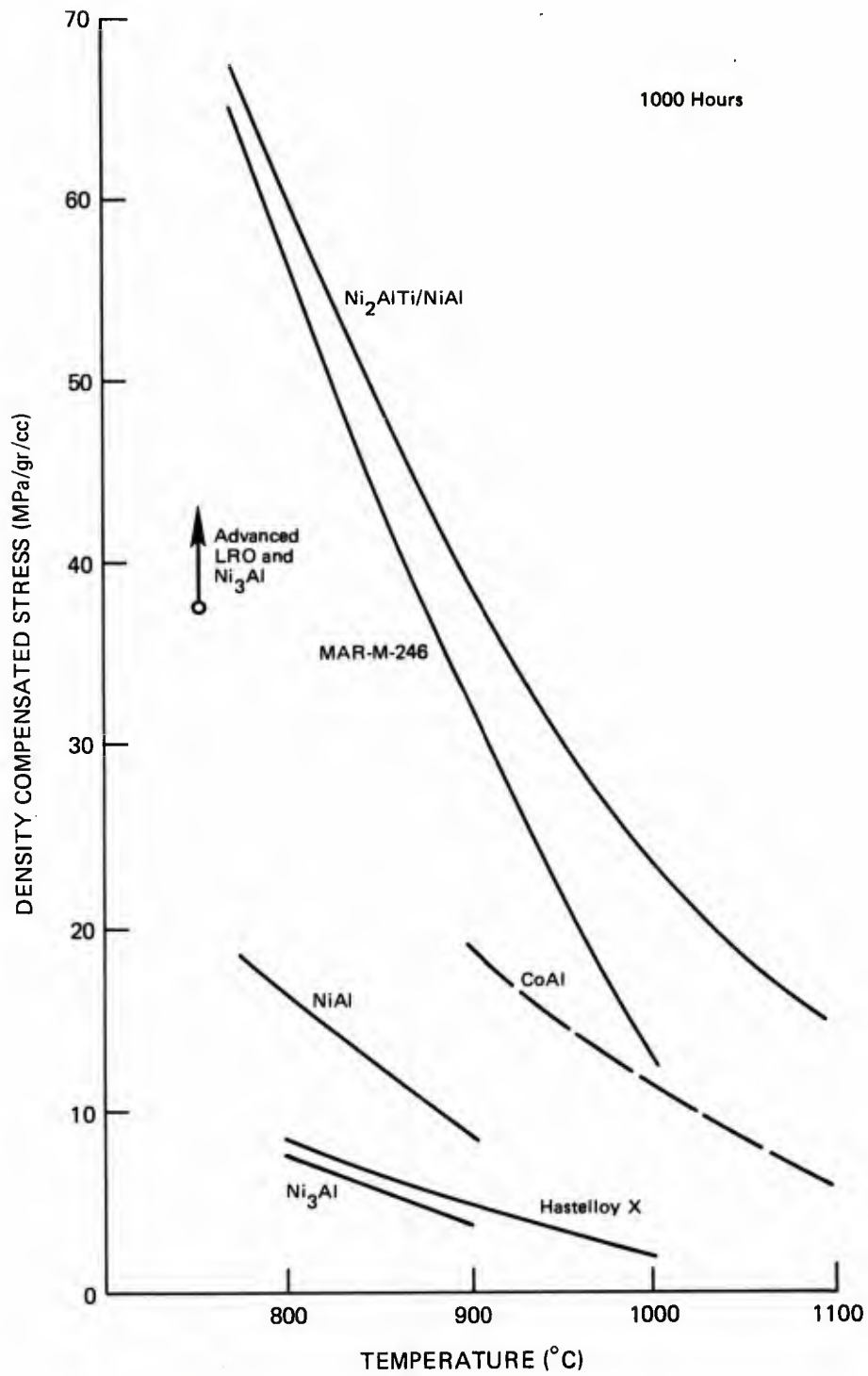
FIGURE 26 Comparative density compensated stress-rupture behavior of several alloys.

Laboratory, Oak Ridge, Tennessee, 1983; Aerospace Structural Metals Handbook, 1984). Available creep data are summarized in Table 5. The limited available data also indicate that the ductile ordered alloys can exhibit good fatigue behavior and good resistance to crack propagation (Figure 10 and 11).

The alloys under consideration in this report offer the greatest apparent potential for applications where their good strength at elevated temperature can be used most advantageously. However, the good oxidation resistance at elevated temperatures of the Ni_3Al-base alloys also may create important applications.

Required Engineering Properties Development Program

In view of the cost and time involved in developing the large body of data necessary to qualify a material for advanced defense system applications, it is recommended that a phased program be undertaken. The intent of the first phase is to produce sufficient data of a screening type to serve as the basis for engineering trade-off studies to assess the potential cost and performance advantages of these alloys in specific applications. If, at the conclusion of this phase, incentives appear sufficient, a second phase of data generation should be undertaken. This phase should include evaluation of the properties of some typical production lots of material and development of sufficient data for the performance of detailed engineering studies to precisely quantify cost and performance advantages. If clear incentives remain at the conclusion of this second phase, the final phase of detailed material qualification should be undertaken. This phase would include development of all information required for specifications, detailed statistical assessments of the material property variability, identification of the influence of fabrication on properties, etc. The activities recommended for each of these phases are as follows:

Phase I--Screening tests on experimental alloys with emphasis on physical properties (modulus, expansivity, conductivity, density), tensile properties, creep-rupture, creep-fatigue, toughness, crack growth, and corrosion behavior (particularly sulfidation/hot corrosion).

Phase II--Characterization testing of experimental and production materials representing several product forms. The emphasis should be on more extensive characterization of properties studied in Phase I as well as studies of effects of multiaxial stress states, product anisotropy, feasibility of joining, and compatibility with a wide range of relevant corrosion environments.

Phase III--Extensive testing of multiple production heats representing all relevant product forms and processing routes. Development of sufficient mechanical property data to permit adequate statistical characterization of all required properties. Development of wide ranging product, process, and joining specifications.

It is assumed that testing in Phase I will be on available experimental heats of material. In addition to the generation of basic physical and

tensile property data, creep rupture, creep fatigue, and cyclic crack growth information must be generated since these properties tend to determine the usefulness of materials in elevated temperature applications. The data generated should be sufficient to at least allow the alloys to be ranked, with respect to strength, relative to other currently available engineering materials. Useful test data probably will lie in the 700 to 1000°C temperature range with tests lasting up to perhaps 1000 hours.

Preliminary characterization of toughness is also viewed as important in Phase I since materials with very poor toughness often are constrained in their engineering utility. Some measure of K or J toughness as a function of temperature in the room temperature to 1000°C range is desirable for this purpose. Similarly, there are some indications that the ductile ordered alloys may, in some cases, have an unusually high susceptibility to crack growth, and such susceptibility, if confirmed, might well limit the engineering utility of the materials. Accordingly, it is important to do some preliminary crack growth characterization at least under fatigue conditions. Finally, because some of the ductile ordered alloys of particular interest have a high nickel content, it is important to characterize their corrosion behavior--particularly in the saline, sulfiding, hot corrosion environments found in many gas turbine applications. Some preliminary screening testing in such environments should be performed.

In Phase II, testing should move toward evaluation of production materials--as well as more extensive evaluation of earlier experimental lots. Data should be generated from at least one production-sized heat of material. It also should be assured that a sampling of applicable product forms is included. Sufficient data should be generated to allow some preliminary assessment of statistical behavior. In addition, preliminary studies of the effects of product form on property anisotropy should be performed and assessments of behavior under multiaxial loading conditions and the feasibility of machining and joining should be completed.

By the time this phase is undertaken, some relevant applications for the alloy systems should have become clear; therefore this testing phase should also involve a preliminary assessment of the compatibility of materials with relevant corrosion environments. Metallurgical stability also must be demonstrated. The influence of long times at elevated temperature under stress on critical strength properties, ductility, and phase stability must be determined.

Phase III basically involves generation of sufficient test data to fully qualify the material for high-reliability advanced defense system applications. Mechanical and physical properties should be determined from three or more production heats of material. This involves not only extensive mechanical property data generation but also the evaluation of a full range of applicable product forms, the development of detailed materials and process specifications, and so on. Reproducible properties and characteristics must be demonstrated from several heats of material using the ultimate product forms intended for use.

SCIENTIFIC DATA

The incidence of order in alloys affects most properties, including the mechanical, electrical, and magnetic properties. Because the changes in properties can be large and because changes in order can be manipulated through control of composition and/or processing conditions, there has developed considerable potential to further exploit these alloys for practical purposes. The actual use of ordered alloys dates back many centuries; current scientific understanding has evolved over the past 60 years (Westbrook 1974). Despite this rich history of work with ordered alloys, there are many aspects of ordering behavior, and its relationship to properties, that remain poorly understood. The intent here is to highlight those areas of research and development that are deemed important to establishing the scientific base needed to further develop ordered alloys as useful engineering materials. An important emphasis of these observations will be the long-term potential of an improved science base to make the processes of structural alloy development more efficient and economical.

In addition, it must be realized that the development of the currently available ductile ordered alloys grew out of scientific programs. The programs at Wright-Patterson and at Oak Ridge have depended very strongly on a scientific foundation that was painstakingly developed for many years before these new alloys were considered.

Phase Diagrams

Although an understanding of phase equilibria underlies all work with ordered alloys and will be discussed later in other contexts, it is important to emphasize that there is considerable need for classical phase diagram determinations for portions of many binary ordering systems as well as for the more complex, but highly practical, cases of ternary and higher order alloys on which little systematic work has been done. It also should be noted that, in many instances, earlier work should be examined in light of the current understanding of phase transformations, particularly the occurrence of precursor transformations and metastable transformation products. Future work will certainly be facilitated by the improved electron, x-ray, and other instrumentation and techniques currently available.

The iron-aluminum system provides an example of the uncertainties that exist for many phase diagrams. There is only partial agreement about the low-temperature region encompassing Fe_3Al and incomplete definition of the high-temperature regions (Figures 27 and 28). Also, little has been done to define the effects of ternary additions to Fe-Al alloys.

More work is needed to define phase equilibria in binary as well as in ternary and higher order ordering systems. This type of work should be encouraged as an important adjunct to alloy development work.

Degree of Order

Ordered phases commonly exist in a less than perfectly ordered state. These deviations from perfect order can be expressed statistically as order
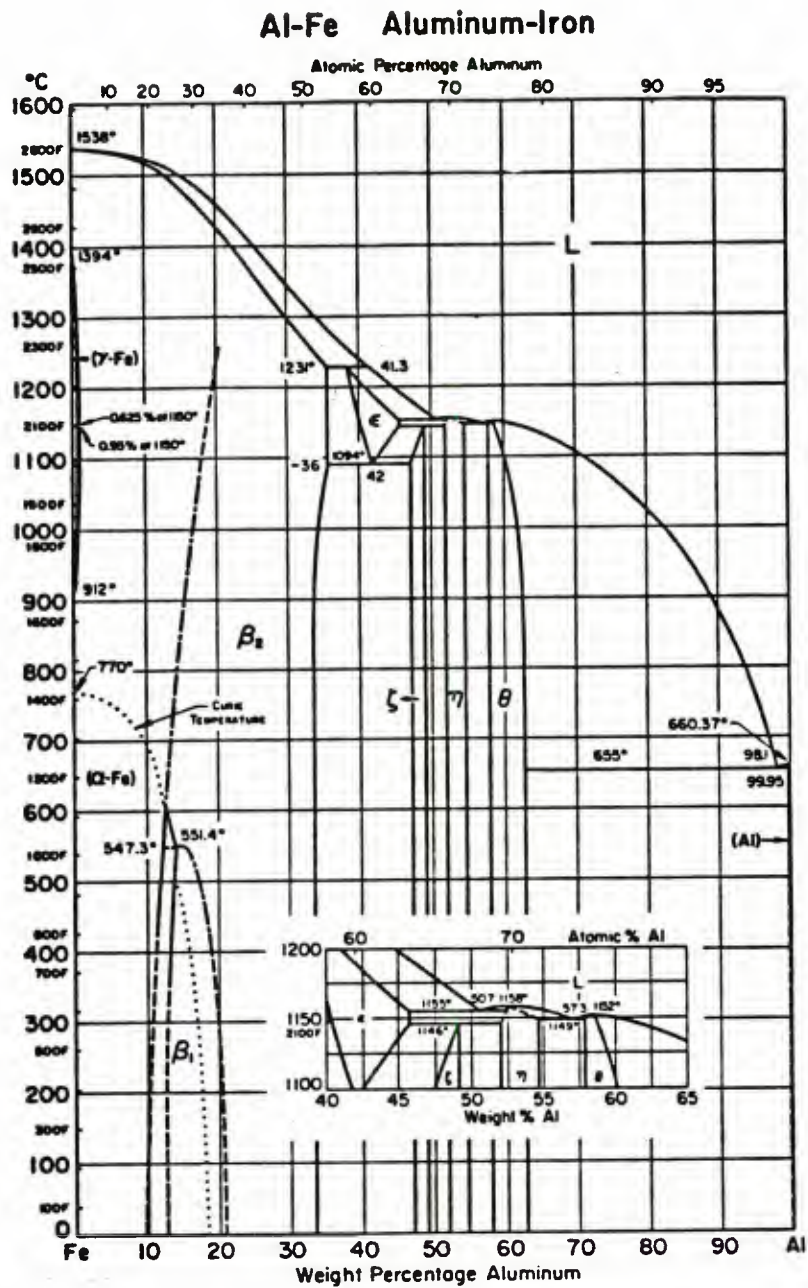
FIGURE 27 Fe-Al phase diagram (American Society for Metals 1973).
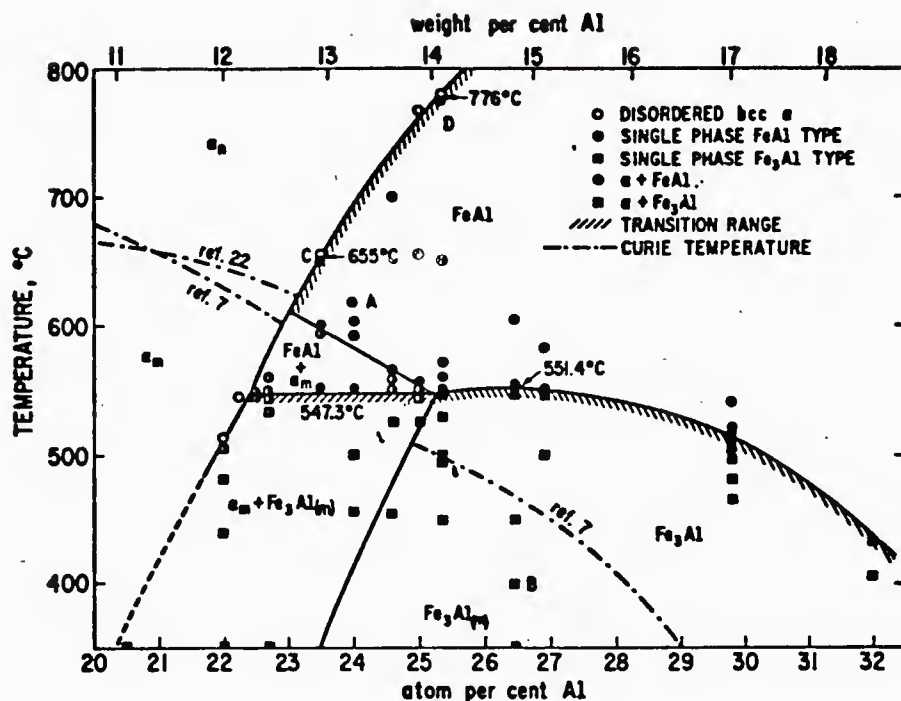
FIGURE 28 Fe-Al phase diagram compiled by Swann and co-workers (1972). For added detail see Allen and Cahn (1975, 1976a, and 1976b).

parameters defining the sublattice occupancies within the structure. Experimentally, order parameters are determined most conveniently and directly by computing the intensity of superlattice reflections, which derive from the occurrence of the order, relative to the fundamental ·reflections, which are independent of order (Barrett and Massalski 1980). Where order is not long range and represents short-range deviations from a state of randomness, short-range-order parameters, or pair probabilities, can be used to describe the atomic arrangement. These can be determined from measurements of diffuse scattering (Cohen 1970).

Of interest here is the fact that the properties of ordered phases are sensitive to changes in the degree of order. For many ordered alloy phases, changes in temperature may cause transformations to disordered phases or new ordered phases, but the degree of order may change well before the temperature of transformation.

An additional area of interest relates to the comments made about phase diagrams. The solubility limit for alloy additions to binary-ordered phases is usually unknown, and, in many cases, the site occupancies associated with

particular alloying elements also are unknown. For example, it can be noted that in more complex structures, such as the DO_3 structure of Fe_3Al shown in Figure 29 (refer to Figure 27), there are several types of sublattice sites available and that the addition of certain elements favoring particular sublattice sites may enhance properties while other choices may result in much smaller, or even deleterious, effects on properties. Of course, the solubility limits may vary considerably with the particular sublattice as well as with the competition for sites between solutes for the case of multiple alloy additions. For certain alloys, site occupancy information can be determined by means other than diffraction. One example is the use of Mossbauer spectroscopy to examine atomic configurations, as has been done with iron and titanium aluminides (Cranshaw 1977, Huffman and Fisher 1967).

TYPE I SITES ON I SUBLATTICE
TYPE II SITES ON II SUBLATTICE
TYPE III SITES ON III SUBLATTICE
TYPE IV SITES ON IV SUBLATTICE
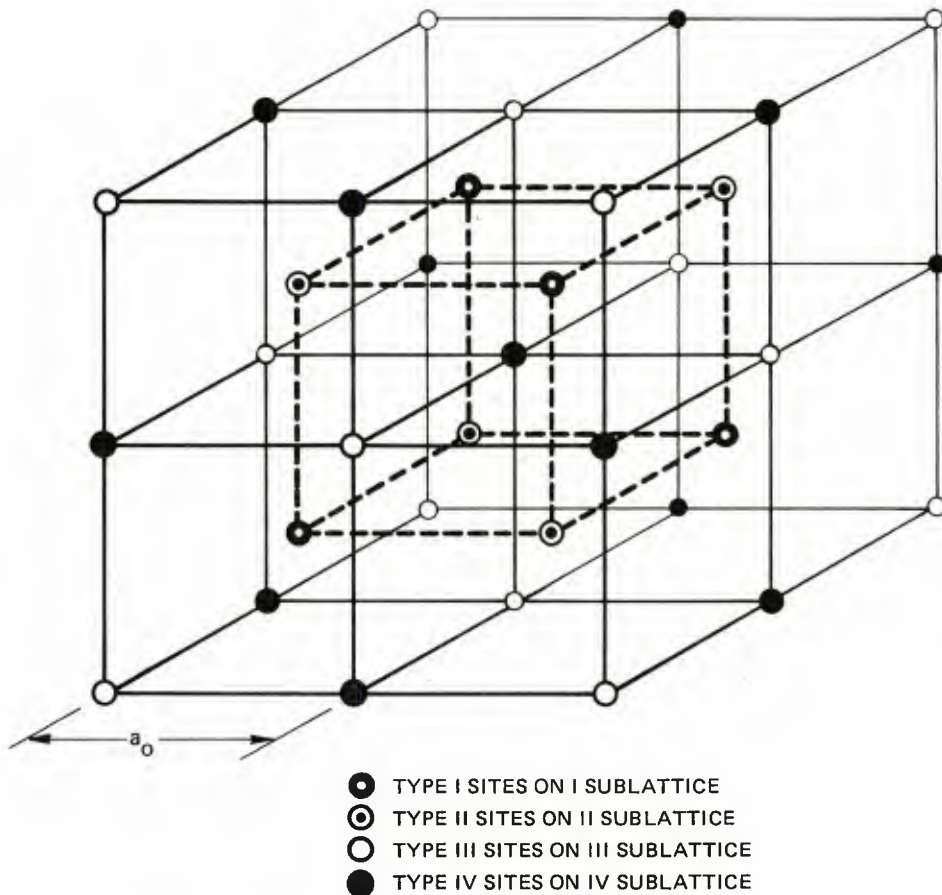
FIGURE 29 Generalized unit cell appropriate for description of DO_3, $L2_1$, and B2 superlattices. B atoms are confined to Type II sites for A_3B and DO_3 structure and to Types I and II for AB with B2 structure (Marcinkowski and Brown 1961).

In considering the degree of order it also is important to recognize the effects of deviations from stoichiometry on the properties of ordered phases. In a number of systems, changes in composition can cause formation of defect solid solutions where vacancies are introduced onto a sublattice rather than a wrong atom type. Similarly, the effects of alloy additions can vary greatly for positive and negative deviations from stoichiometry, as evidenced by the recent success of boron additions in ductilizing Ni_3Al only for alloys with less than 25 at% Al (Liu et al. 1983).

Finally, it must be recognized that the kinetics of ordering vary greatly among ordered phases and, further, that little is known about the effect of alloy additions on the kinetics. Because of the wide variety of processing conditions ranging from rapid solidification to conventional casting, with or without mechanical working, a high degree of order cannot be assumed and must generally be introduced by a specific ordering heat treatment.

An improved understanding of the degree of order and ordering kinetics and how these are affected by chemical composition is needed. It is particularly important that the evaluation of properties include specification of the chemistry, degree of order, and detailed thermal-mechanical processing history.

Dislocations, Antiphase Boundaries, and Stacking Faults

Because ordering changes the translation vectors of the lattice, the motion of normal dislocations creates disorder. However, dislocations can move in combined arrays, or superlattice dislocations, separated by APBs or other faults so as to preserve order. It is the interplay between various superlattice and single dislocation processes as a function of temperature and other variables that determines the mechanical properties of many ordered materials. Complete characterization of the Burgers vectors and slip systems has only been done for certain ordered phases with much less information about changes caused by alloying. In those cases where dislocations dissociate into partial dislocations, the superlattice dislocations become more complex involving both APBs and a variety of stacking faults. The balance between the APB and stacking fault energies, therefore, determines the nature of the dislocations, the slip systems, and the mechanical properties through effects such as the restriction or enhancement of the ability to cross slip (Pope and Ezz 1984). Particular combinations of partial dislocations also can provide low energy faults and a means of forming deformation twins in ordered structures (Mikkola and Cohen 1966).

APBs also can be formed thermally because alloy phases order by a random choice of sublattice for the ordering process. As these ordered regions, or antiphase domains, which differ only in sublattice choice, grow and impinge, the interface formed creates an APB. Depending on some unknown relationships between a variety of factors including the crystallography and the APB energy, these APBs can be planar or crystallographic in nature or assume random orientations.

In addition to the important role of APBs in affecting dislocation behavior, such as cross slip, it is important to note that the kinetics of

APD growth and/or the thermal history can cause the APD size to be very small. This can influence both the properties and the ability to detect the order by some techniques. Also, as with any interface, there exists the potential for segregation to APBs.

The interrelationships between the nature of the dislocations, stacking faults, and deformation-induced APBs probably determine the mechanical properties of ordered alloys. However, there are several areas of mechanical behavior that await a unified interpretation based on these relationships. For example, there is as yet no common basis for understanding the anomalous temperature dependence of the strength of many ordered phases (Pope and Ezz 1984), although the phenomenon appears to be reasonably well understood in Ni_3Al.

Fundamental work on the deformation behavior of ordered alloys is needed. This includes not only the binary systems, but also ternary and higher order alloys where little systematic work has been done. In addition, more information is needed about APB energies, superlattice dislocations, and APD structures.

Grain Boundary Characteristics

Probably the most important factor limiting the engineering use of many ordered alloys, particularly those of interest for elevated-temperature applications, has been poor ductility. In many cases it appears that these ductility problems stem from segregation to grain boundaries and/or the intrinsic properties of grain boundaries. For example, single-crystal Ni_3Al is quite ductile at room temperature, but polycrystalline Ni_3Al is quite brittle. Recently Liu and co-workers (1983), following the lead of some Japanese workers (Aoki and Izumi 1979), have been able to ductilize polycrystalline Ni_3Al by addition of boron, which probably segregates to the grain boundaries. In this work it has been suggested that the boron compensates for intrinsically weak grain boundaries in Ni_3Al by acting as an electron donor to electron-deficient regions at the grain boundaries. Unfortunately, the addition of boron to other brittle aluminides appears to be of little benefit.

It also should be noted that there is good reason to believe that many grain boundary effects are sensitive to stoichiometry. With Ni_3Al it was found that boron was effective only for compositions with less than 25 at% Al (Liu et al. 1983). Much remains to be learned about these effects, and it may be that the unique structural nature of intermetallics will create the potential for a substantial contribution to the general understanding of grain boundary effects.

There appears to be good potential for improving the mechanical properties of many intermetallics under monotonic and cyclic loading through a better understanding of grain boundary effects. The importance of intrinsic grain boundary properties, as well as the fact that segregants can be beneficial or harmful, has been demonstrated. There is a strong need for more controlled experiments in this area.

Other Areas

There are several other areas in which work is needed. These will be commented on briefly below.

The enhancement of creep resistance and the interpretation of creep measurements, as well as other processes such as high-temperature oxidation and coating behavior, will require an improved understanding of diffusion in ordered alloys. Little quantitative information about diffusion in binary ordered alloys is available, and only a limited amount of work has been done on the more complex ternary and higher order alloys.

Related to the area of diffusion is the need for additional work on point defects in ordered alloys. Point defects are important, not only because they occur in defect solid solutions formed at off-stoichiometric compositions in some phases, but also because of the role they play in determining ordering kinetics, general mass transport, and phase stability.

Finally, one class of ordered alloys has been of scientific interest for some time, but it has not been exploited for practical use. These are the long-period superlattice phases in which a periodic APB structure of very fine spacing forms within the domains of the normal ordered structure (Barrett and Massalski 1980). The stability and occurrence of this type of order has generally been related to electron energy effects arising from the interaction between the Fermi surface and the Brillouin zone (Sato and Toth 1961 and 1962). The period, or APB spacing, at a constant temperature depends largely on the electron-to-atom ratio and can range from a few to several tens of atom spacings. Little has been done to evaluate the properties of these materials.

The Potential Impact of Improving the Science of Ordered Alloys

Current approaches to the discovery and development of new structural alloys are, of necessity, largely empirical and Edisonian in nature. This will continue to be the case in the near future, with the role of science being mostly interpretive rather than predictive. However, for a variety of reasons, not the least of which are the efficiency and cost of the current methods, it might be expected that other approaches will be sought and developed. Fortunately, it now appears that there is a great potential for science to make stronger inputs to alloy design and development. This has developed largely because of rapid advances in computing capabilities and in instrumentation for structural and chemical characterization.

Of particular interest here are the tremendous advances to be expected from quantum mechanical calculations of ordered alloys. It is now generally agreed that these calculations soon will be sufficiently accurate to be useful as input to further calculations dealing with real alloys (Connolly and Williams 1983, Gyorffy and Stocks 1983, Stocks 1983, Williams et al. 1979, Williams et al. 1980). The results of the quantum mechanical calculations will generally yield the energies, lattice parameters, and elastic constants, at absolute zero, for perfectly ordered arrangements of two or more atom types. Energies also will be available for clusters of a few atoms within a lattice of "average" atoms. It will be important that

materials researchers take advantage of the results of these calculations by developing means of calculating the properties of real alloys under a variety of real conditions. In addition, it will be extremely important that a variety of parameters, such as phase transition temperatures as a function of composition, are available to facilitate refinement and testing of the calculations. Because ordered alloys can be defined structurally by experiment and, further, because the structures can be controlled through heat treatment, the impact of the theoretical calculations described above will be greatest for these alloys. It should be expected that the future will bring predictive capabilities to complement and act as an efficient screening tool for the usual methods of alloy development.

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6

PROCESSING OF DUCTILE ORDERED ALLOYS

INTRODUCTION

Recent breakthroughs in the development of ductile ordered alloys have
resulted in research focused on the development of a variety of ordered
alloys including aluminides (Liu and Koch 1982) and $(FeNi)_3$-V type
materials (Liu 1973 and 1979). This work has focused primarily on
mechanical property behavior as a function of composition and heat
treatment. As these materials mature, consideration must be given to the
manufacturing technology required for the fabrication of useful hardware.
At the present time, consideration of processing techniques is generally
limited to the generation of small lots of material for characterization
purposes. In the future, attention should be given to the production and
subsequent processing of commercial lots of material. The processing
technology is extremely important because most of the cost associated with
incorporating a new material system into either military or commercial
systems is related to process optimization and finalization (Stephens and
Tien 1983). In anticipation of this need to consider production
requirements, current methods used for the manufacture of material for
characterization purposes were reviewed.

CURRENT PRODUCTION METHODS

The literature on the various production processes employed for the
preparation of ordered alloys for alloy development and characterization
studies was surveyed. This review revealed that:

1. A wide variety of methods have been employed for the wide range of
compositions under investigation. To date, there has been no focus on any
particular method for fabricating any particular class of ordered material.

2. The methods can be classified into three generic types as shown in Figure 30, which represents a flow diagram or process routing for the preparation of ordered material. Starting with the initial melting operation, the three generic types include casting, deformation processing, and powder metallurgy.

3. In all cases, the amounts of material made were relatively small (generally less than 50 pounds) and did not represent production type quantities.

4. With the exception of the casting approach, some type of subsequent secondary processing such as machining, forming or forging, or joining (welding, brazing, diffusion bonding) would be required for the fabrication of useful hardware.

With these general points in mind, a brief description of the routing steps is presented below.

Melting

Each of the three process routings begins with the preparation of alloy ingot or melt stock. In general, either vacuum induction or arc melting
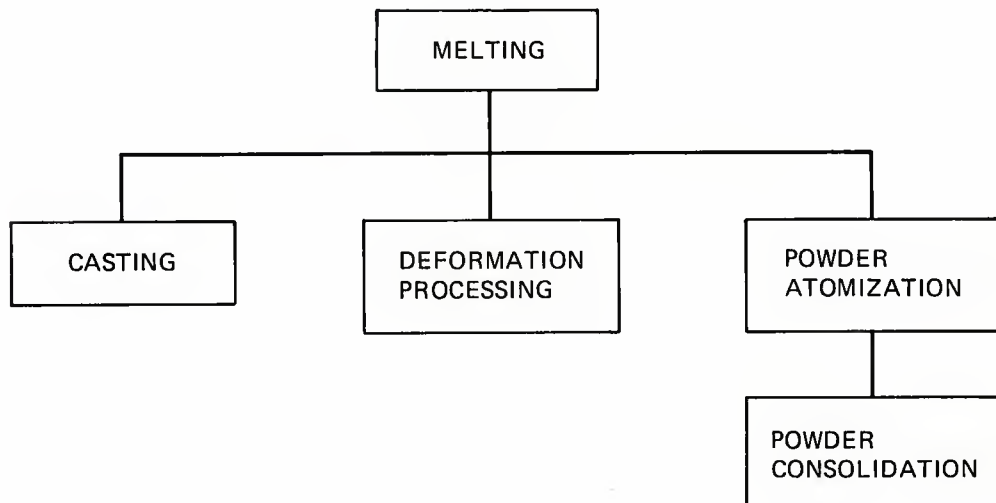
FIGURE 30 Current process routing for the production of ordered alloys.

under some type of protective atmosphere was used to produce the initial ingot material. Vacuum melting was used for such materials as Cu_3Au (Kear and Wilsdorf 1962, Chien and Starke 1975), Cu_2NiZn (Van der Wegen et al. 1982), and Ni_3Al (Thornton et al. 1970, Davies and Stoloff 1965). Arc melting was used for a wide variety of materials including Ni_3Al (Guard and Westbrook 1959), $FeCoV/Fe_3Al$ (Stoloff and Davies 1964a), Mg_3Cd (Stoloff and Davies 1964b), AgMg (Westbrook and Wood 1962-63), Ni_3Ge/Fe_3Ge (Suzuki et al. 1980), $Ni-Ni_4Mo$ (Nesbit and Laughlin 1980), and beta brass (Shea and Stoloff 1974). High-purity elemental constituents were used as the starting stock and, in general, argon gas was used as the protective atmosphere for the arc melting operations. A variety of crucibles, including ceramic and graphite containers, was used to produce round ingot shapes or buttons. In general, less than 50 pounds, and in most cases less than 10 pounds, of alloy was produced. There appear to have been few problems with off-chemistry compositions, and good yields generally were achieved. In summary, little difficulty has been encountered during the melting of small quantities of ordered alloy compositions.

Casting

Subsequent preparation of cast specimens for mechanical property evaluations has been directed towards obtaining either an equiaxed microstructure, as in studies involving ordered intermetallic phases in superalloys (Copley and Kear 1967), or single crystals in the $Ni_3(Al,Nb)$ (Ezz et al. 1982) and $Ni_3(Al,W)$ (Kuramoto and Pope 1978) systems. In all cases, vacuum casting was employed and equiaxed microstructures were obtained through conventional solidification techniques in which heat is extracted from the molten metal by radiation through the mold material. The single-crystal castings also were produced in vacuum, and the mold containing the molten metal was withdrawn through a thermal gradient at a controlled rate to achieve directional solidification. Orientation control was achieved by using either a single-crystal seed or a grain selector configuration to obtain the desired orientation. It is recognized that the development of casting techniques was not a major thrust in these investigations. It can therefore be concluded that the casting approach represents a potential method for manufacturing components from ordered alloys.

Deformation Processing

Deformation processing of ordered alloys involves a variety of operations performed subsequent to the preparation of the melt stock material. The primary purpose is to obtain a homogeneous composition and a uniform microstructure. Vacuum-melted ingots have been subjected to hot (Kear and Wilsdorf 1962, Davies and Stoloff 1965) and cold (Van der Wegen et al. 1982) rolling, and arc-melted ingots have been subjected to hot (Stoloff and Davies 1964a, 1964b) and cold (Nesbit and Laughlin 1980) rolling, hot extrusion (Westbrook and Wood 1962-63), and upset forging (Shea and Stoloff 1974). The rolling operations resulted in sheet or plate of varying thickness, the hot extrusion operations generally resulted in cylindrical bar stock, and the upset forging operations resulted in pancake type configurations. These operations were conducted on alloys canned or clad

with various materials in order to aid heat retention during processing, avoid surface cracking during processing, and protect the various alloys from environmental degradation during heating to the working temperature.

It must be emphasized that the deformation processing operations cited here were performed for the purpose of supplying small laboratory lots of material. They were not conducted as part of a systematic program to select optimum process routings that achieve maximum material yield or optimum mechanical properties. The various process variables, including cladding material, reduction ratio (for extrusion), reduction per pass (for the rolling operations), and working temperature, were selected on the basis of previous experience with similar types of material. The overall results of these studies were quite encouraging, however, in that the workability potential of a wide variety of compositions by a wide variety of processing methods has been demonstrated. These results suggest that plate or bar stock material can be produced by normal deformation processing methods.

Powder Metallurgy Processing

PM processing of ordered alloys also is under investigation because it can offer a number of important advantages. In addition to the savings resulting from increased materials utilization compared to conventional ingot metallurgy, PM allows the formulation of structures with nonequilibrium phases, an extension of the range of solid solubility, a refinement of resultant grain size, and a suppression of grain boundary segregation. As a result of these advantages, PM processing of ordered alloys has received considerable attention.

PM processing involves two basic steps: powder atomization and powder consolidation. A number of atomization approaches have been employed for the production of ordered alloys. These approaches feature a range of cooling rates between 1000°C/sec and 1,000,000°C/sec. The lower cooling rates generally are associated with the rotating electrode process (REP) and higher rates with inert gas (argon) atomized powder. REP has been used for the preparation of titanium aluminide powders (Sastry and Lipsitt 1977, Mendiratta and Lipsitt 1980) while argon atomization has been used for the preparation of iron aluminide powders (Vedula 1983). The higher rates are generally associated with rapid solidification rate (RSR) processing, which is achieved by centrifugal atomization in combination with forced convective cooling, and with melt-spun ribbons. The RSR process has been used for the preparation of various materials including iron aluminides (Chatterjee and Mendiratta 1982), and melt spinning has been used for the preparation of various materials including Ll_2 compounds of the type Ni-Al-X(X=Cr, Mn, Fe, Co, or Si) (Inoue et al. 1983). Each of the processes offers advantages associated with either process economics, production scale-up capability, or the ability to achieve extremely high cooling rates. At this point, no preferred atomization process has evolved for the preparation of ordered alloy powders. Characterization of powders made from a wide variety of alloys and processes is under way. As is the case for deformation processing of ordered alloys, no systematic investigation has yet been conducted relating powder processing parameters to overall process economics or mechanical property performance.

Subsequent to atomization, the powders must be consolidated for further evaluations. Although a number of consolidation approaches are available, most of the work done to date on ordered alloy powders involves either vacuum hot pressing or hot extrusion. Vacuum hot pressing can be used to form a net shape or near net shape, but hot extrusion must be followed by subsequent fabrication to form a useful component. Again, no systematic investigations of the hot pressing or hot extrusion operations have been conducted to optimize process economics or mechanical property performance. Characterizations thus far of the melt-spun ribbons have been limited to the ribbons themselves, but studies involving pulverized ribbons subjected to subsequent PM consolidation processes are in progress (Ray et al. 1983). Although the results of PM studies conducted to date on ordered alloys are of a preliminary nature, they do suggest that this type of processing approach can be applied to this class of materials.

PRODUCTION SCALE-UP CONSIDERATIONS

In order to address the issues that must be considered when scaling-up for large-scale production of a new material, a specific processing approach must be selected. On the basis of the studies conducted to date on ordered alloys, some potential has been demonstrated for processing a wide variety of compositions by a wide variety of processing methods. Although no single processing approach has evolved for any particular composition, an assessment can be made regarding what is currently known about the manufacture of these materials. In general, three major issues must be addressed: scale-up to larger, production size quantities; process optimization to reach a compromise between process economics and mechanical property performance; and secondary fabrication approaches necessary to manufacture production hardware. These issues are discussed below for each of the steps shown in Figure 30.

Melting

The major issue regarding melting of ordered alloys is related to the maximum size production heat that can be produced with the desired chemistry. Ingots of melt-stock material of specialty alloys such as ordered alloys are qualified on the basis of their chemistry specifications, which control not only the major element additions but also the tramp or impurity levels. The specific major element chemistry ranges for ordered alloys will be established as more knowledge is obtained regarding the effects of off-chemistry. Because on-line chemical analysis is now routinely performed during vacuum-induction melting, off-chemistry with regard to the major element additions is not anticipated to be a problem. This may not be the case, however, for other kinds of melting operations, and certain of the ordered alloy systems may present particular chemistry problems. For example, the properties of some alloys change greatly with small changes in stoichiometry. This may make the control of composition more difficult than in ordinary alloys. Impurity levels also may present a problem, particularly if high superheat or pour temperatures are required. Higher temperature melting operations usually are associated with a greater degree of crucible/metal reactivity and can result in degradation of the ceramic filters currently used to remove nonmetallic inclusions.

Scale-up to production size heats of ductile ordered alloys also may require secondary processing steps for macrostructural and microstructural control. In many instances, primary ingots cannot be directly hot worked because of coarse and nonuniform grain sizes, shrinkage pipes, and relatively high degrees of macrosegregation and microsegregation, which represent problems particularly in alloys featuring complex chemistries. Vacuum arc remelting has overcome many of these problems and, in addition to developing more uniform composition, properties and structure, offers the capability to improved purity. A recent innovation in remelting, termed the VADER process (Boesch et al. 1982), offers significant advantages compared to vacuum arc remelting including a decrease in energy consumption for comparable melt rates and significantly finer and more uniform grain sizes to enhance subsequent deformation processing. Although these secondary melting operations have not yet been applied to the ductile ordered alloy class of materials they do represent potential methods for improving the quality of primary ingots.

Process yield is also an important consideration. For example, a process yield of 90 percent or greater usually is obtained when producing superalloys, and any melting process that results in yields of less than 90 percent would have limited applicability.

Casting

The manufacture of castings of new materials such as the ordered alloys requires extensive process optimization to ensure high yields. Important considerations are the specific gating/risering systems to be employed for the specific configurations, the mold systems that must be used, the number of individual castings that can be made per mold, and the specific casting procedure that must be used. So far, none of these considerations has been addressed with regard to cast ordered alloys.

Casting yield is a direct function of the types of defects encountered during the production operation. In general, the quality requirements increase with the complexity of the casting operation, being more stringent with single-crystal castings than with equiaxed castings. Equiaxed castings are evaluated in terms of x-ray (for internal porosity and inclusions), Zyglo penetrant inspection (for surface-connected porosity and surface inclusions), dimensional tolerance (including core shift for the production of castings with internal cooling passages), and mechanical properties of specimens machined from actual components. Columnar-grain and single-crystal castings also undergo this type of inspection and an additional step involving etching to check for the presence of off-axis grains (for columnar-grained castings) and surface equiaxed grains (for single-crystal castings). Single-crystal castings also undergo inspection for orientation determination. Significant costs are associated with this quality assurance activity and, when combined with the cost of the casting processes themselves, account for approximately 90 percent of the component costs. This means that since materials constitute less than 10 percent of the final cost, the use of smaller quantities of critical or strategic materials in some of the new ordered alloys cannot be expected to result in dramatically reduced costs.

Deformation Processing

The production scale-up considerations related to deformation processing concern economics, capital equipment needs, and mechanical property requirements. Process economics generally are controlled by process yields. Most material losses during processing occur due to the rejection of material that contains edge or surface defects. Losses also are encountered in the extrusion operation due to the need to crop off nose and tail sections to remove undeformed or nonuniformly deformed material in these locations. In general, material yields in excess of 90 percent are usually required in order to achieve attractive process economics. Another concern regarding process economics is the degree of control required to accomplish the desired deformation. This is usually referred to as the processing "window" and includes the specific tolerances that must be maintained in terms of process temperature, amount of reduction, and time required. All of these parameters influence the uniformity of the deformation response throughout the material. Process costs escalate as the "window" narrows, and no data on the size of this "window" for the newly developed ordered alloys are yet available.

Capital equipment needs relate to the size of the equipment needed to accomplish the desired deformation. As size requirements increase, the number of vendors able to accomplish the work with the desired quality decreases. A potential problem area here may be the long lead times associated with scheduling the work. This situation is already prevalent in the aircraft industry where lead times of more than one year are not uncommon.

The scale-up problem associated with mechanical property performance is related to achieving the desired property levels in large section size. Extrusion barstock and plate specifications call for minimum mechanical property requirements to be met as a function of various specimen orientations. In scale-up operations, there usually is a decrease in mechanical property performance due to section size effects. This is related in part to the significantly slower cooling rates obtainable in large section sizes that have an adverse effect on the morphology of the various strengthening phases in the microstructure. Increasing the cooling rate from the heat treatment temperature by the use of various quenching media (hot salt, for example) can up-grade the mechanical property response, but care must be taken so that quench cracks are not developed. This problem may not arise with the scale-up of single-phase ordered alloys but may be present in ordered alloys featuring a second phase.

Powder Metallurgy Processing

In discussing the scale-up of PM processing, both powder atomization and powder consolidation must be considered. These two areas will be discussed separately below.

Both the production capability and the quality of the resulting powder are important considerations. Production size capability is intimately associated with economics, and a relatively large-scale production

capability now exists for the slower-cooling-rate powders produced by REP and inert gas atomization. In fact, inert gas atomization is currently in use for the production of large quantities of nickel-base superalloy powders used for disk applications in the aircraft industry. The atomization costs for these powders generally are less than $2 per pound. Atomization costs for the REP powder are approximately $6 per pound. With regard to the faster-cooling-rate powders and ribbons produced by the RSR and melt-spinning processes, large-scale production quantities of these materials are not yet available. Efforts are in progress, however, to scale-up facilities to produce larger quantities of these materials. No cost projections are yet available. At the current time, then, large scale-up PM processing of ordered alloys would be limited to the PREP and inert gas atomization processing.

Powder quality concerns are related primarily to the presence of defects in the powders and their effects on low cycle fatigue, fracture toughness, and fatigue crack growth. The evolution of damage-tolerant designs and retirement-for-cause concepts in the aircraft industry has placed stringent requirements on powder quality. As a result of these requirements, powder producers now have strict control of powder chemistry, both major elements and tramp or impurity levels. Powder lots also are inspected by water elutriation and metallographic techniques to determine the presence of extraneous particles such as ceramic particles from mold/metal reaction, reactive defects such as parts of O-ring seals, and cross alloy contamination resulting from the atomization of various alloy compositions. Currently, efforts are being made to minimize the use of ceramics during the atomization of high-temperature powders. Since the presence of ceramic particles in ordered alloys are also expected to be very deleterious, similar quality control procedures will be required for their powder production.

The vacuum hot pressing and hot extrusion consolidation approaches for the ordered alloys involve scale-up considerations similar to those discussed previously for deformation processing (i.e., process economics, capital equipment needs, and mechanical property requirements). An additional requirement, however, is the need to maintain powder purity during any consolidation operation. This is related to the possible contaminant pick-up during powder transfer and handling and subsequent loading into vacuum hot pressing or hot extrusion cans. In certain instances all-inert powder handling is thus specified for critical rotating components.

Secondary Fabrication

With the exception of cast-to-size components, some type of secondary processing will be required for the fabrication of useful hardware from ordered alloy material. These secondary processing procedures could include machining, forging or forming, and some type of bonding fabrication operation such as welding, brazing, or diffusion bonding. To date, systematic studies of these techniques involving process optimization and definition have not been done on the ordered alloys. Some preliminary work has been conducted on welding of nickel aluminides (private communication

with S. A. David, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1983) and (Ni,Fe)$_3$(V,Ti) long-range-ordered material (Braski 1983). The effects of electron beam welding parameters (for the aluminides) and gas tungsten arc (GTA) welding parameters (for the long-range-ordered material) on weld quality were characterized. For both types of materials, conditions were identified that resulted in crack-free welds. In more general terms, the incorporation of joining fabrication operations in the overall processing sequence for ordered alloys also will have to address section size effects on joint quality and mechanical property response as well as the effects of phase transformations in those systems featuring multiphase microstructures. Until such studies have been conducted, no realistic assessment can be made as to whether the ordered alloys as a class of materials would present any more difficulties than do the currently used materials.

SUMMARY-PROCESSING

A wide range of processing methods have been employed for the preparation of material for the initial characterization of ordered alloys, including such primary processing techniques as alloy melting, casting, deformation processing, and PM methods. These efforts have demonstrated that considerable flexibility exists for the manufacture of ordered alloys in bar and sheet form as well as in simple cast configurations. There have been no systematic studies of these approaches with regard to achieving an optimized process in terms of economics and mechanical property performance. In addition, except with casting, the primary processing must be followed by some type of secondary operation in order to fabricate useful hardware. Up to now only limited efforts have been directed towards evaluation of these secondary operations. Once specific alloy compositions evolve from the current work in progress on ordered alloys and possible defense applications can be identified, studies can be directed toward process optimization and scale-up. Until these studies are conducted, a realistic assessment cannot be made of the difficulty of fabricating components from ordered alloys relative to current bill-of-materials.

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APPENDIX

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

MARTIN J. BLACKBURN received his B.A. (1958) and Ph.D. (1962) from the University of Cambridge. Upon graduation he joined the Boeing Company and worked for ten years in the Scientific Research Laboratory. After a year (1972-3) as Visiting Scientist at the Aerospace Research Laboratories, Wright-Patterson Air Force Base, he joined Pratt and Whitney Aircraft. There he is currently Manager of Structural Metals and Process Development. During his career he has worked on a wide variety of materials including extensive development activities in the field of ordered alloys. He published widely in earlier years and holds a number of patents including two for ordered alloys based on the titanium aluminides.

THOMAS F. KEARNS received his B.S. in Metallurgical Engineering from Columbia University in 1940. He is currently a member of the Research Staff at the Institute for Defense Analyses, where he is involved in advisory studies and analyses for the Department of Defense and Defense Advanced Research Projects Agency in the area of materials and structures research and development. From 1941 to 1980 Mr. Kearns was a Materials Engineer with the Department of the Navy. His major activities with the Navy were in the area of engineering control of materials in Naval aircraft and equipment and in planning and sponsorship of research and development in materials, structures, and aerodynamics related to Naval aircraft. He also served as National Liaison Officer for Materials with the Organization for Economic Cooperation and Development, Chairman, Structures and Materials Panel, AGARD/NATO, and was a member of the Advisory Technical Awareness Council of the ASM. He is a Fellow of the American Society for Metals and a recipient of the ASM Burgess Award and the Navy Superior Civilian Service Award.

CHARLES S. KORTOVICH joined TRW in 1964 and has been closely involved with research in the area of high temperature superalloys, including isothermal forging dies, computerization studies in investment castings, trace element effects, hot isostatic pressing of castings, and the development of superalloys through PM techniques for blade/vane and disk applications. He is currently responsible for evaluation and monitoring of strategic elements, physical metallurgy (alloy development, powder metallurgy, and coating development), and fracture mechanics and mechanical property behavior evaluation of high temperature materials. Dr. Kortovich received his Ph.D. from Case Western Reserve University in 1973. He is a member of the American Society for Metals and the American Institute of Mining, Metallurgical, and Petroleum Engineers, of which he is currently a member of the Gas Turbine Panel of the High Temperature Alloys Committee. He holds several patents in the area of processing high temperature materials for gas turbine applications.

DONALD E. MIKKOLA has served on the faculty of the Michigan Technological University for twenty years and is currently Professor of Metallurgical Engineering. His research is concerned with structure-property relations in materials as studied with x-ray diffraction and electron microscopy, with current emphasis on ordered alloys, high strain rate deformation, and

comminution. He received his Ph.D. from Northwestern University in 1964. He is a member of the Engineering Accreditation Commission of the Accreditation Board for Engineering and Technology.

DAVID P. POPE received his B.S. degree from the University of Wisconsin in 1961 and his M.S. and Ph.D. degrees from the California Institute of Technology in 1962 and 1967, respectively. Dr. Pope has been a member of the faculty of the University of Pennsylvania since 1968 and is now Professor of Materials Science and Engineering and Associate Dean for Undergraduate Education in the School of Engineering and Applied Science. He is a member of the American Institute of Mining, Metallurgical, and Petroleum Engineers and the American Society for Metals. His recent publications have been in the fields of deformation behavior of ordered alloys and on composition-mechanical behavior relationships in steels.

NEIL E. PATON received his B.S. and M.S. degrees in Mechanical Engineering from the University of Auckland, New Zealand in 1961/1962 and his Ph.D. in Materials Sciences from M.I.T. in 1969. He is currently the Director of Materials Engineering and Technology at the Rocketdyne Division of Rockwell International. Dr. Paton has been engaged in the study of physical metallurgy and deformation of metals for the past 20 years and has authored or co-authored over 55 technical papers and given more than 60 technical presentations based on his research. He is also the holder of 10 patents. Dr. Paton was awarded a Titanium Metal Corporation of America Fellowship in 1965 and the Rockwell International Engineer of the Year Award in 1976. He is a member of The Metallurgical Society/American Institute of Mining, Metallurgical, and Petroleum Engineers and is currently Chairman of the Titanium Metallurgy Committee of TMS. He has served on several National Academy of Sciences committees and was Chairman of the 1983 Gordon Conference on Physical Metallurgy.

DAVID I. ROBERTS is currently Manager of Materials Engineering and Testing at GA Technologies (formerly General Atomics) in San Diego, California. He is responsible for programs to select and qualify materials for gas cooled reactors, for fusion reactor development programs, and for nuclear space power and related advanced energy generation system development. Mr. Roberts received his MIM degree from the University of London in 1960. He is a registered Professional Engineer in the state of California and a member of the American Society for Metals, the American Society of Mechanical Engineers, the National Association of Corrosion Engineers, and the Institute of Met. (United Kingdom).

MICHAEL J. STALLONE received his BME degree from Polytechnic Institute of Brooklyn in 1953 and completed the General Electric's Advanced Engineering Program in 1956. At General Electric Company he conducted analytical and experimental studies in low cycle fatigue, bucket creep, and life prediction methods. He has held a series of managerial positions responsible for providing advanced analytical methods in various aspects of structural and vibration analysis. In his present position as Manager of Applied Stress and Dynamics, he is responsible for advanced analysis and methods development for blade aeromechanics, rotor and structural vibration, and life design of engine blading and structures. In 1968 he was awarded the

General Electric Company Perry T. Edbert Memorial Award for Outstanding
Technical Contribution. He is a member of the American Institute of
Aeronautics and Astronautics and the American Society of Mechanical
Engineers.

NORMAN S. STOLOFF received his Ph.D. in Metallurgy in 1961 from Columbia
University. He is currently Professor of Materials Engineering at
Rensselaer Polytechnic Institute. Dr. Stoloff's research interests include
fatigue of composite materials, microstructure and properties of nickel-base
superalloys, and deformation and fracture of intermetallic compounds. He is
a member of and has been active on various technical committees of the
American Institute of Mining, Metallurgical, and Petroleum Engineers, the
American Society for Metals, and the American Society for Testing and
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